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## (54) INK-JET RECORDING PAPER

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide ink-jet recording paper which contains fine solid particles dispersed in a hydrophilic binder, has high ink absorption power, keeps the fragility of a membrane even when stored in an atmosphere of low humidity, and is capable of high quality ink-jet recording.

**SOLUTION:** In ink-jet recording paper, at least one ink absorption layer containing fine solid particles and polyvinyl alcohol is provided on a support, and in at least one ink absorption layer, the weight ratio of the particles to polyvinyl alcohol is 2-200. A layer containing the particles contains polyvinyl alcohol of at most 1000 average molecular weight and polyvinyl alcohol of at least 2000 average molecular weight.

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CLAIMS

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[Claim(s)]

[Claim 1] The ink jet record form with which the layer containing this solid-state particle is characterized by 1000 or less polyvinyl alcohol and average degree of polymerization containing [ average degree of polymerization ] 2000 or more polyvinyl alcohol in the ink jet record form with which it has at least one-layer ink absorption layer containing a solid-state particle and polyvinyl alcohol, and at least one layer of this ink absorption layer contains a solid-state particle two to 200 times by the weight ratio to the total amount of polyvinyl alcohol on a base material.

[Claim 2] The ink jet record form according to claim 1 characterized by said solid-state particle being a solid-state particle chosen from the silica whose mean particle diameter of a primary particle is 7–80nm, respectively, a calcium carbonate, an alumina, hydrated alumina, or a magnesium silicate.

[Claim 3] The ink jet record form according to claim 1 characterized by said solid-state particle being the silica compounded by the gaseous-phase method the mean particle diameter of a primary particle is 7–30nm.

[Claim 4] An ink jet record form given in any 1 term of claims 1–3 to which said average degree of polymerization is characterized by the amount of 1000 or less polyvinyl alcohol being [ average degree of polymerization ] 1 – 30 % of the weight in a weight ratio to 2000 or more polyvinyl alcohol.

[Claim 5] It has at least one layer of ink absorption layers which contain a solid-state particle and polyvinyl alcohol at least as a hydrophilic binder on a base material. It is the ink jet record form whose weight ratio of the solid-state particle to the hydrophilic binder of at least one layer of this ink absorption layer is two to 200 times. The ink jet record form with which the hydrophobic organic compound or glass transition temperature of 40 degrees C or less is characterized by this ink absorption layer containing the oil droplet as which the melting point is chosen from polymeric latex 40 degrees C or less five to 50% of the weight to a solid-state particle.

[Claim 6] The ink jet record form according to claim 5 characterized by the mean diameter of said oil droplet being 0.05–0.5 micrometers.

[Claim 7] The ink jet record form according to claim 5 or 6 characterized by said solid-state particle being a solid-state particle chosen from the silica whose mean particle diameter of a primary particle is 7–80nm, respectively, a calcium carbonate, an alumina, hydrated alumina, or a magnesium silicate.

[Claim 8] The ink jet record form according to claim 5 or 6 characterized by said solid-state particle being the silica compounded by the gaseous-phase method the mean particle diameter of a primary particle is 7–30nm.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the ink jet record form which has improved especially ink absorptivity about the ink jet record form which records using water color ink.

#### [0002]

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] As an ink jet record form used by this ink jet recording method, also when a printing dot laps [ that a color tone is brightly skillful and absorption of ink ] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [ the concentration of a printing dot is high, and ] beyond the need, and it is required that the circumference should be smooth and should not fade etc.

[0004] Since it becomes nonuniformity, and the color of each other in the border area of a color which a drop causes a HAJIKI phenomenon on an ink jet record form, and is different spreads and it is easy to reduce image quality greatly in case the liquid ink drop of two or more colors laps and is recorded, when especially ink rate of absorption is slow, it is required to give ink absorptivity high as an ink jet record form.

[0005] In order to solve these problems, very many techniques are proposed from the former.

[0006] As the pigment in \*\*\*\*-ed indicated by the ink jet record form which carried out humidity of the coating for surface treatment to the low size stencil paper indicated by JP,52-53012,A, the ink jet record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, and JP,56-157,A The ink jet record form containing non-colloid silica powder, the ink jet record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The ink jet record form which has two hole distribution peaks indicated by JP,58-110287,A, The ink jet record form which consists of a vertical two-layer porous layer indicated by JP,62-111782,A, The ink jet record form which has the indeterminate form crack indicated by JP,59-68292,A, 59-123696, the 60-18383 official report, etc., The ink jet record form which has the impalpable powder layer indicated by JP,61-135786,A, 61-148092, the 62-149475 official report, etc., JP,63-252779,A, JP,1-108083,A, 2-136279, The ink jet record form containing the pigment which has the specific physical-properties value indicated by 3-65376, 3-27976, etc., or a particle silica, JP,57-14091,A, 60-219083, 60-210984, 61-20797, 61-188183, JP,5-278324,A, 6-92011, 6-183134, 7-137431, The ink jet record form containing particle silicones, such as a colloid silica indicated by 7-276789 etc., And JP,2-276671,A, a 3-67684 official report, 3-215082, A large number are known for the ink jet record form containing the hydrated alumina particle indicated by 3-251488, 4-67986, 4-263983, the 5-16517 official report, etc.

[0007] Especially, an ink absorbing layer can absorb ink, or when it is the layer (henceforth an

opening layer) which has many openings for holding, ink absorptivity is good, there are few blots of the boundary section, and a quality image can be recorded.

[0008] And since that capacity may change under high-humidity/temperature especially while this opening saves, it is desirable that a solid-state particle from which an opening does not change into an opening layer is included.

[0009] To make a solid-state particle contain and make an opening form in an opening layer, it is required in order for making a hydrophilic binder contain to make a stable coat form. However, if there are too many additions to the solid-state particle of a hydrophilic binder, the opening made to form between the solid-state particle itself or a solid-state particle will be taken up, or there will be a problem of this hydrophilic binder itself swelling in early stages of ink absorption at the time of ink absorption, plugging up an opening layer, and reducing ink absorptivity, and that amount used will be limited.

[0010] According to examination of this invention persons, the ratio of the addition of the hydrophilic binder to a solid-state particle is understood that it is required to increase 2 to 200 times in general at a weight ratio.

[0011] It has the fault containing the solid-state particle of such a high ratio that the brittleness of a coat is inferior, carrying out layer measles, and when saved especially under damp, a detailed crack condition is generated on the front face of an ink absorption layer. When ink jet record is performed in such an ink jet record form, ink will spread along with this cracked line, and image quality will be reduced remarkably.

[0012]

[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned actual condition, and the purpose of this invention is to offer [ have the high ink absorptivity containing the solid-state particle distributed in the hydrophilic binder, for the brittleness of a coat not to fall, even if it is the case where it saves under damp, but ] the ink jet record form in which high-definition ink jet record is possible.

[0013]

[Means for Solving the Problem] The above-mentioned purpose of this invention is attained by the following configurations.

[0014] 1. Ink jet record form with which layer containing this solid-state particle is characterized by 1000 or less polyvinyl alcohol and average degree of polymerization containing [ average degree of polymerization ] 2000 or more polyvinyl alcohol in ink jet record form with which it has at least one-layer ink absorption layer containing solid-state particle and polyvinyl alcohol, and at least one layer of this ink absorption layer contains solid-state particle two to 200 times by weight ratio to total amount of polyvinyl alcohol on base material.

[0015] 2. Ink jet record form given in said 1 characterized by said solid-state particle being solid-state particle chosen from silica whose mean particle diameter of primary particle is 7-80nm, respectively, calcium carbonate, alumina, hydrated alumina, or magnesium silicate.

[0016] 3. Ink jet record form given in said 1 characterized by said solid-state particle being silica compounded by gaseous-phase method mean particle diameter of primary particle is 7-30nm.

[0017] 4. Ink jet record form given in said any 1 term of 1-3 to which said average degree of polymerization is characterized by 1000 or less amount of polyvinyl alcohol being [ average degree of polymerization ] 1 - 30 % of the weight in weight ratio to 2000 or more polyvinyl alcohol.

[0018] 5. It Has at Least One Layer of Ink Absorption Layers Which Contain Solid-state Particle and Polyvinyl Alcohol at Least as a Hydrophilic Binder on Base Material. It is the ink jet record form whose weight ratio of the solid-state particle to the hydrophilic binder of at least one layer of this ink absorption layer is two to 200 times. The ink jet record form with which the hydrophobic organic compound or glass transition temperature of 40 degrees C or less is characterized by this ink absorption layer containing the oil droplet as which the melting point is chosen from polymeric latex 40 degrees C or less five to 50% of the weight to a solid-state particle.

[0019] 6. Ink jet record form given in said 5 characterized by mean diameter of said oil droplet being 0.05-0.5 micrometers.

[0020] 7. Said 5 characterized by said solid-state particle being solid-state particle chosen from silica whose mean particle diameter of primary particle is 7-80nm, respectively, calcium carbonate,

alumina, hydrated alumina, or magnesium silicate, or ink jet record form given in 6.

[0021] 8. Said 5 characterized by said solid-state particle being silica compounded by gaseous-phase method mean particle diameter of primary particle is 7-30nm, or ink jet record form given in 6.

[0022] Hereafter, this invention is explained to a detail.

[0023] Although the solid-state particle which the ink jet record form of this invention contains can use a well-known solid-state particle conventionally in an ink jet record form, its non-subtlety particle is desirable.

[0024] it is used for this purpose — well-known, if a non-subtlety particle is carried out at an ink jet — for example Precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, Clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, Zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, White inorganic pigments, such as the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide, etc. can be used.

[0025] Such a non-subtlety particle may be added in the condition of being used into a binder after homogeneity has distributed having also formed secondary floc with the primary particle, and having distributed in the binder.

[0026] On the other hand as an example of an organic particle, polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, or melamine resin is mentioned.

[0027] It is desirable to use an inorganic solid-state particle from the point that an opening layer with comparatively high voidage is obtained in this invention. It is desirable that the point that high glossiness and high image concentration are easy to be obtained especially to a solid-state particle is a solid-state particle chosen from a silica, a calcium carbonate, an alumina, hydrated alumina, or a magnesium silicate.

[0028] As a silica system particle preferably used in the ink jet record form of this invention, various kinds of well-known silica system particles can be conventionally used by the ink jet.

[0029] For example, the synthetic silica compounded by wet or the gaseous-phase method, colloidal silica, and the silica of the configuration of the porosity silica arbitration which a primary particle condenses and forms the secondary particle can be used. As such an example, for example, the synthetic amorphous silica indicated by JP,55-51583,A, 56-148583, etc., For example, the silica ultrafine particle compounded by the gaseous-phase method indicated by JP,60-204390,A, The synthetic indeterminate form silica containing the fluorine indicated by JP,60-222282,A, The synthetic indeterminate form silica in which surface treatment was carried out by the silane coupling agent indicated by JP,60-224580,A and 62-178384, For example, the spherical silica indicated by JP,62-183382,A and 63-104878, The synthetic silica particle whose Na<sub>2</sub>O content indicated by JP,63-317381,A is 0.5 % of the weight or more, The specific surface area indicated by JP,1-115677,A The synthetic silica particle more than 100m<sup>2</sup>/g, The synthetic silica particle which was indicated by JP,62-286787,A and by which alumina surface treatment was carried out, The synthetic silica particle by which surface treatment was carried out with salts, such as calcium, Mg, or Ba indicated by JP,1-259982,A, The colloidal silica oil absorption was indicated to be by a 180ml [ /g ] or more composition silica particle and JP,57-14091,A, The cationic colloidal silica indicated by JP,60-219084,A, JP,6-92011,A, 6-297830, and 7-81214, And the colloidal silica which connected in the shape of [ which was indicated by JP,5-278324,A and 7-81214 ] a rosary, or branched can be mentioned.

[0030] However, in order to obtain high glossiness and the high amount of openings, it is desirable to use the ultrafine particle silica whose mean particle diameter is 7-80nm. This silica particle may be the object which cation conversion could be carried out in the front face, and was processed by aluminum, calcium, Mg, Ba, etc.

[0031] As a calcium carbonate preferably used in the ink jet record form of this invention For example, JP,57-12486,A, 57-129778, 58-55283, The precipitated calcium carbonate which has specific surface area in the specification indicated by 61-20792, The needle pillar-shaped calcium carbonate indicated by JP,63-57277,A and JP,4-250091,A, The calcium-carbonate particle which

the specific needlelike primary particle indicated by JP,3-251487,A condensed, and formed the secondary particle, the needle which has the specific oil absorption indicated by JP,4-250091,A and 4-260092 — a pillar-shaped prismatic crystal Argo night calcium carbonate, the spherical precipitated calcium carbonate indicated by JP,7-40648,A are mentioned.

[0032] In this case, since high glossiness and the high amount of openings can be obtained, it is desirable to use the calcium-carbonate particle whose particle size is about 7-80nm.

[0033] Tabular is desirable although the magnesium silicates preferably used by this invention may be an indeterminate form particle, a globular shape, and tabular any. The mean particle diameter of a tabular magnesium silicate is expressed with the diameter when converting this into a circle in quest of a tabular average projected area, and its 7-80nm particle is desirable.

[0034] The alumina or hydrated alumina preferably used by this invention may be crystallinity, or may be amorphous, and a configuration can use the object of the configuration of arbitration, such as an indeterminate form particle, a spherical particle, and a needlelike particle.

[0035] The mean particle diameter of various kinds of above-mentioned inorganic solid-state particles measures the average projected area when photoing it with an electron microscope, and expresses the diameter when converting this into a circle.

[0036] As for especially the above-mentioned solid-state particle preferably used by this invention, it is desirable that it is that whose mean particle diameter of a primary particle is 7-80nm.

[0037] When primary particle diameter is less than 7nm, handling nature is difficult, and the fall of gloss tends to become remarkable in exceeding 80nm.

[0038] The above-mentioned solid-state particle content layer needs to contain a hydrophilic binder in respect of coat formation in the ink jet record form of this invention.

[0039] As a hydrophilic binder generally used for an ink jet record form Gelatin or a gelatin derivative, a polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), A pullulan, polyvinyl alcohol, or its derivative (about 20,000 or more have desirable average molecular weight), A polyethylene glycol (100,000 or more have a desirable mean molecular weight), a carboxymethyl cellulose, Hydroxyethyl cellulose, a dextran, a dextrin, polyacrylic acid, and its salt, An agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, A polyalkylene oxide system copolymerization nature polymer given in locust bean gum, an alginic acid, gum arabic, a pullulan, JP,7-195826,A, and 7-9757, Although polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has a water-soluble polyvinyl butyral, or a carboxyl group and a sulfonic group given in JP,62-245260,A, etc. are known, it sets to this invention. It is required in the viewpoint of smeariness prevention high ink absorptivity and high glossiness, and control of further curl and under highly humid to contain polyvinyl alcohol at least.

[0040] In polyvinyl alcohol here, the polyvinyl alcohol by which cation denaturation was carried out in addition to the polyvinyl alcohol usually said, such as a partial saponification object or a full saponification object of polyvinyl acetate, is also contained.

[0041] As for whenever [ saponification / of the above-mentioned polyvinyl acetate ], 70 – 99% of thing is preferably used by this invention 60 to 100%.

[0042] Moreover, the desirable polyvinyl alcohol by which cation denaturation was carried out is obtained by saponifying the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical.

[0043] As an ethylenic unsaturated monomer which has a cationic radical For example, TORIMECHIRU-(2-acrylamide -2, 2-dimethyl ethyl) ammoniumchloride, TORIMECHIRU-(3-acrylamide -3, 3-dimethyl propyl) ammoniumchloride, N-vinyl imidazole, N-vinyl-2-methylimidazole, N-(3-dimethylaminopropyl) methacrylamide, Hydroxyl ethyl trimethylammonium chloride, TORIMECHIRU-( methacrylamide propyl) ammoniumchloride, N-(1 and 1-dimethyl-3-dimethylaminopropyl) acrylamide, etc. are mentioned.

[0044] 0.1-10-mol% of the ratio of the cation denaturation radical content monomer of cation denaturation polyvinyl alcohol is desirable to vinyl acetate, and is 0.2-5-mol % more preferably. Moreover, whenever [ 60 – 100% of ], whenever [ saponification / of cation denaturation polyvinyl alcohol ] is desirable, and it is 70 – 99% more preferably.

[0045] In the ink jet record form of this invention, the ratio to the hydrophilic binder of the solid-

state particle which forms an opening layer is a weight ratio, and needs to be two to 200 times. It becomes, and a hydrophilic binder swells at the time of ink absorption that it is easy to produce the problem of everything accompanying thickness being too thick at the time under of 2 double in order for the rate of a void ratio formed to absorb the amount of the maximum ink completely small, the ink rate of absorption of an opening layer is reduced, and the image quality acquired is reduced.

[0046] On the other hand, in exceeding 200 times, it it adopts the below-mentioned various means, the brittleness of a coat deteriorates greatly and high-definition ink jet record becomes impossible.

[0047] It is 2.5 to 100 times the desirable ratio of this, and is especially 3 to 50 times the desirable ratio of this.

[0048] Moreover, as a solid-state particle, when a desirable gaseous-phase method silica is used especially, desirable ratios are 3-20.

[0049] In order to improve the coat brittleness accompanying this, since the opening layer of the ink jet record form of this invention contains the solid-state particle of a high ratio especially to a hydrophilic binder like the above \*\* This solid-state particle content layer [ whether 1000 or less polyvinyl alcohol and average degree of polymerization contain / average degree of polymerization / 2000 or more polyvinyl alcohol and ] Or that thing [ that any one is filled at least ] in which \*\* solid-state particle content layer contains an oil droplet five to 50% of the weight to a solid-state particle is required.

[0050] In the above and \*\*, it is desirable to use more nearly high-polymer polyvinyl alcohol for formation of the stable coat which cannot produce a crack easily, and a coat with good extent which is that average degree of polymerization uses 2000 or more polyvinyl alcohol independently from this viewpoint is obtained. Conversely, especially when only the polyvinyl alcohol of low molecular weight is used, in the coat containing many solid-state particles, it is easy to produce a crack in the desiccation process after spreading.

[0051] However, when a crack with a coat minute when average degree of polymerization uses only 2000 or more polyvinyl alcohol is not lost completely and it saves under an elevated temperature after spreading desiccation, the brittleness of a coat falls, and it becomes easy to produce a crack in a coat especially under low humidity conditions.

[0052] this invention persons find out that this problem is improved because average degree of polymerization uses together 1000 or less low degree-of-polymerization polyvinyl alcohol to the high polyvinyl alcohol of average degree of polymerization, and result it in the 1st this invention.

[0053] 3000 or more things of average degree of polymerization are [ average degree of polymerization ] desirable also especially of the 2000 or more polyvinyl alcohol. Since the liquid of the concentration which the solubility of polyvinyl alcohol falls and is made into the purpose becomes impossible easily as it generally high-polymerization-izes although the upper limit of average degree of polymerization is not limited from the point of brittle amelioration of a coat, as for average degree of polymerization, especially generally, 4000 or less are [ 5000 or less ] desirable.

[0054] As for average degree of polymerization, 400 or less are [ especially a desirable thing / 500 or less ] the most desirable [ average degree of polymerization ] on the other hand among 1000 or less polyvinyl alcohol.

[0055] Although especially the minimum of average degree of polymerization is not limited, it is usually 200 or more.

[0056] It is desirable that the amount of 1000 or less polyvinyl alcohol is [ average degree of polymerization ] 1 – 30% in a weight ratio to 2000 or more polyvinyl alcohol for average degree of polymerization. If the effectiveness of this invention becomes that it is hard to be obtained substantially and it exceeds 30% in being less than 1%, the plasticity of the coat after spreading desiccation becomes easy to get worse, and especially crack formation will increase or it will become easy for an adhesive property with a base material to fall. Especially the desirable range is 2 – 20%.

[0057] In the above-mentioned \*\*, it is roughly divided into two kinds of things as an oil droplet which an ink absorption layer contains.

[0058] The 1st [ the ] is the case where the melting point is the oil droplet in which said oil droplet has a hydrophobic organic compound 40 degrees C or less, and the 2nd thing is the case where said oil droplet is [ glass transition temperature ] polymeric latex 40 degrees C or less.

[0059] solubility [ usually as opposed to / in the oil droplet of the 1st type / water at a room temperature ] — less than [ 0.1% % of the weight ] — it is 0.01 or less % of the weight especially preferably, and the melting point is a hydrophobic organic compound 40 degrees C or less.

[0060] A hydrophobic polymer 40 degrees C or less is mentioned for the organic compound with which such a hydrophobic organic compound is known as a usual hydrophobic high-boiling point organic solvent, and the melting point.

[0061] as the above-mentioned hydrophobic organic compound — for example, phthalic ester (for example, dibutyl phthalate —) Phosphoric ester, such as dioctyl phthalate and di-isodecyl phthalate For example, (tricresyl phosphate, trioctylphosphate), etc., fatty acid ester (butyl stearate and a sebacic acid screw (2-ethylhexyl) —) Ethylene glycol distearate, glycero RUTORI butyrate, etc., Amides (N and N-diethyl lauryl amide, N, and N-diethyl-2-(2, 5-G t-amyl phenoxy) butaneamide etc.) Ether (ethylene glycol dibutyl ether, DESHIRU ether, dibenzyl ether, etc.), a silicone oil, a liquid paraffin, etc. can be mentioned.

[0062] Moreover, the melting point is mentioned for Pori (2-ethylhexyl methacrylate), poly butyl methacrylate, copoly (butyl acrylate / hydroxyl ethyl methacrylate: 90/10), polyvinyl acetate, polyvinyl propionate, copoly (butyl acrylate / t-butyl acrylate / 2-ethylhexyl methacrylate / styrene: 60/20/10/10), etc. as a hydrophobic polymer 40 degrees C or less, for example.

[0063] The polymer whose average molecular weight is 5000 to about 100,000 as the above-mentioned hydrophobic polymer is used preferably. In the case of the polymer exceeding 100,000, it is hard coming to form the oil droplet of a particle by approaches, such as emulsification distribution mentioned later.

[0064] Emulsification distribution is preferably carried out under existence of a surfactant into a hydrophilic binder by the high-speed homogenizer, a high-pressure homogenizer, etc., and the above-mentioned hydrophobic organic compound is used. Under the present circumstances, it is desirable to carry out emulsification distribution under existence of low-boiling point organic solvents, such as ethyl acetate, propyl acetate, a methyl ethyl ketone, an acetone, N and N, and dimethylformamide, etc., although minuter \*\*\*\* is formed.

[0065] Moreover, although the organic compound to which the melting point exceeds 40 degrees C with other hydrophobic organic compounds (for example, an ultraviolet ray absorbent, a fluorescent brightener, an image stabilizer, etc.) at the time of this emulsification distribution can also be used together, it is desirable that 50% of the weight or more of the organic compound which forms \*\*\*\* preferably of the melting point is a compound 40 degrees C or less.

[0066] On the other hand, polymeric latex 40 degrees C or less is polymeric latex to which the polymerization of the 2nd glass transition temperature was carried out by the emulsion-polymerization method, for example, a styrene-butadiene copolymer latex, a polyacrylic ester system latex, a polymethacrylic-acid-ester system latex, a vinyl acetate system latex, an ethylene-vinyl acetate system latex, etc. are used preferably.

[0067] As an example of the above-mentioned polymer latex, for example, styrene / butadiene latex (7/3), a polyvinyl acetate latex, vinyl acetate / ethylene latex (9/1), vinyl acetate / ethyl methacrylate latex (5/5), a vinyl chloride/ethyl acrylate (3/2), an ethyl acrylate / methyl acrylate / HEMA (5/4/1), styrene / butyl acrylate / HEMA (1/6/3), a silicon latex, etc. can be mentioned. In the above, a \*\*\*\* ratio expresses a mole ratio and HEMA expresses hydroxyl ethyl methacrylate.

[0068] As for the mean particle diameter of various kinds of above-mentioned oil droplets, it is desirable that it is 0.05-0.5 micrometers. When the size of an oil droplet is 0.05 micrometers or less, it becomes, or it is easy to reduce the brittle amelioration effectiveness, and an oil droplet becomes being easy to become unstable. Moreover, when the size of an oil droplet exceeds 0.5 micrometers, it becomes easy for gloss to fall.

[0069] The above-mentioned oil droplet is required for using it five to 50% of the weight to the solid-state particle which an ink absorption layer contains to acquire the effectiveness of this invention.

[0070] When the ratio to the solid-state particle of an oil droplet is less than 5 % of the weight, the

brittle amelioration effectiveness of a coat is inadequate, and in exceeding 50 % of the weight, the rate of a void ratio falls, ink absorption capacity falls or the fall of gloss tends to take place.

[0071] Especially the desirable amount used is 10 – 40 % of the weight.

[0072] The ink jet record form of this invention can also have the ink absorption layer containing a solid-state particle and a hydrophilic binder more than two-layer. In this case, although the class or ratio of a hydrophilic binder or a solid-state particle used for the ink absorption layer of these plurality is chosen as arbitration, at least one layer needs to use together two kinds of polyvinyl alcohol with which average degree of polymerization differs like this invention in this layer, or to add the oil droplet of this invention about the case where there is a layer from which the ratio of the solid-state particle to a hydrophilic binder has increased 2 to 200 times.

[0073] In order to pull out especially the effectiveness of this invention to the maximum extent, it is using together using the polyvinyl alcohol with which the above-mentioned average degree of polymerization's differs, and an oil droplet.

[0074] Although the ink jet record form of this invention has at least one-layer ink absorption layer containing an above-mentioned solid-state particle and an above-mentioned hydrophilic binder, it can have a hydrophilic binder layer besides this solid-state particle content layer. Even if such a hydrophilic binder layer has the solid-state particle, it does not need to be, but when there is nothing, in case it is prepared in the side which is preferably separated from a base material from the solid-state particle content layer of this invention in an opening layer, it is desirable from the point of ink rate of absorption to make it 2 micrometers or less of desiccation thickness preferably set to 1.5 micrometers or less.

[0075] Various kinds of additives can be made to contain if needed in the layer of the arbitration by the side of the ink receptiveness layer of the ink jet record form of this invention.

[0076] For example, an ultraviolet ray absorbent given in JP,57-74193,A, a 57-87988 official report, and a 62-261476 official report, JP,57-74192,A, a 57-87989 official report, a 60-72785 official report, The fading inhibitor indicated by a 61-146591 official report, JP,1-95091,A, the 3-13376 official report, etc., An anion, a cation or the various surfactants of Nonion, JP,59-42993,A, The fluorescent brightener indicated by a 59-52689 official report, a 62-280069 official report, a 61-242871 official report, JP,4-219266,A, etc., Various well-known additives, such as lubricant, such as pH regulators, such as a sulfuric acid, a phosphoric acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, and a diethylene glycol, antiseptics, a thickener, a hardening agent, an antistatic agent, and a mat agent, can also be made to contain.

[0077] An inorganic or organic hardening agent can be used as a hardening agent, for example, chromium alum, formaldehyde, a glyoxal, an epoxy system compound, a vinyl sulfone system compound, an acryloyl system compound, s-triazine system compound, N-methylol system compound, a carbodiimide system compound, ethylene imino \*\*\*\*\* etc. can be used.

[0078] Although especially a limit does not have the amount of the spreading solid content by the side of the ink recording surface in the ink jet record form of this invention, 10 – 40 g/m<sup>2</sup> is desirable in general, and 20 – 30 g/m<sup>2</sup> is more desirable. In addition, from the field of prevention of the curl after record image formation, it is good to form as thinly as possible.

[0079] Into the configuration layer of the arbitration by the side of the ink recording surface of this invention, an alkali-metal weak acid salt the poly allylamine of publications, such as the poly cation polyelectrolyte of JP,56-84992,A, a basic latex polymer of JP,57-36692,A, JP,61-58788,A, and a 62-174184 official report, and given in JP,61-47290,A etc. can be used more than a kind as a deck-watertight-luminaire-ized agent of an image.

[0080] As a base material used for the ink jet record form of this invention, a thing well-known as a record form for ink jets can be used suitably conventionally.

[0081] The thing of a property which bears the radiant heat when being able to mention the film which consists of ingredients, such as polyester system resin, diacetate system resin, thoria TESETO system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, a plate, a glass plate, etc. as a transparency base material, for example, and being used as an OHP also in this is desirable, and especially polyethylene terephthalate is desirable. As thickness of such a transparent base material, about

10–200 micrometers is desirable.

[0082] Moreover, what carried out opacification processing of the sheet which consists of common paper, a synthetic paper, resin covering paper, cloth, wood, a metal, etc. as a base material used when there is no transparent need, for example, a plate, and the above-mentioned translucency base material with the well-known means can be mentioned. The so-called White pet which comes to add white pigments to the resin covering paper (the so-called RC paper) which has the polyolefin resin enveloping layer which added white pigments etc. at least to one side of a base paper as an opaque base material, and polyethylene terephthalate is desirable.

[0083] Especially the effectiveness of this invention has large effectiveness, when a base material is non-absorptivity, and transparency or an opaque polyethylene terephthalate base material, and the base material that covered both sides of stencil paper with hydrophobic resin, such as polyethylene, are used especially preferably.

[0084] It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of an ink absorbing layer for the purpose, such as to enlarge bond strength of a base material and an ink television layer. Furthermore, the ink jet record form of this invention does not necessarily need to be colorlessness, and may be the colored record sheet.

[0085] In manufacturing the ink jet record form of this invention, the approach of applying each hydrophilic layer containing an ink receptiveness layer on a base material can be suitably chosen from a well-known approach, and can be performed.

[0086] As a spreading method, the extrusion coat method which uses a hopper the roll coating method, a rod bar coating method, the air-knife-coating method, a spray coating method, the curtain method of application, or given in a U.S. Pat. No. 2,681,294 official report is used preferably.

[0087] The water color ink said by this invention is the following coloring agent and a solvent object, and a record liquid that consists of other additives. Water soluble dye, such as direct dye well-known as a coloring agent at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used.

[0088] As a solvent of water color ink, water and water-soluble, various organic solvents For example, methyl alcohol, isopropyl alcohol, n-butyl alcohol, Alcohols, such as tert-butyl alcohol and isobutyl alcohol; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a ketone-alcohol; tetrahydrofuran, Ether, such as dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, Polyhydric alcohol, such as a diethylene glycol, a glycerol, and triethanolamine; Ethylene glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol methyl (or ethyl) ether and the triethylene glycol monobutyl ether, is mentioned.

[0089] Also in the water-soluble organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, and the triethylene glycol monobutyl ether etc. is desirable.

[0090] As an additive of other water color ink, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust-proofer, etc. are mentioned, for example.

[0091] In order that the wettability to an ink jet record form may make it good, in 20 degrees C, as for water-color-ink liquid, it is desirable that it is 25 – 60 dyne/cm, and it is desirable to have the surface tension of 30 – 50 dyne/cm within the limits more preferably.

[0092]

[Example] Although an example is given and this invention is explained concretely, the embodiment of this invention is not limited to these.

[0093] It painted and dried and the ink jet record form –1 was produced so that humid thickness might be set to 190 micrometers to the printing paper base material for photographs (12% of the weight of anatase mold titanium oxide is contained in the polyethylene layer by the side of an ink absorption layer) which covered 1160g of examples/, and both sides of the stencil paper of m2 with polyethylene in the following coating liquid –1.

[0094] The slide hopper method performed spreading, and after spreading and after cooling at about 10 degrees C and drying for 1 minute by the wind of this temperature, by the 30 degrees C – 45 degrees C wind, it applied for 4 minutes and dried.

[0095]

Coating liquid –1 Pure water (ion exchange water) 950ml Ethanol 30ml 50ml Silica (gaseous-phase method [ primary / an average of / particle diameter is 13nm ] silica) 51g Polyvinyl alcohol 8g (whenever [ average-degree-of-polymerization =3500 and saponification ] = 88%)

Surfactant (AS-1) 0.1g AS-1: It is an ink jet record form as well as the ink jet record form –1 about the ink jet record form which added the organic compound of addition and a comparison for the hydrophobic organic compound of this invention in triisopropyl naphthalene sulfonic-acid sodium, next the ink jet record form –1 as shown in Table 1. – 2–11 were produced. However, with addition of an oil droplet, pure water adjusted the whole quantity of coating liquid so that it might become the same in each ink jet record form. Moreover, as a surfactant, under existence of AS-1, each above-mentioned hydrophobic compound carried out emulsification distribution, and added in polyvinyl alcohol.

[0096]

[Table 1]

記録用紙	添加剤 (融点)	油滴径	添加量
2 (比較例)	流動パラフィン (mp<10°C)	0.3 $\mu$ m	3%
3 (本発明)	#	#	10%
4 (本発明)	#	#	30%
5 (比較例)	#	#	90%
6 (比較例)	D I D P (mp= -53°C)	0.32 $\mu$ m	3%
7 (本発明)	#	#	10%
8 (本発明)	#	#	30%
9 (比較例)	#	#	90%
10 (比較例)	固体パラフィン (mp=60°C)	0.36 $\mu$ m	20%
11 (比較例)	D P P (mp=74°C)	0.28 $\mu$ m	20%

D I D P : ジイソデシルフタレート

D P P : ジフェニルフタレート

表中、添加量はシリカに対する重量比で表した。

記録用紙 : インクジェット記録用紙

[0097] The approach of describing ink absorptivity, coat brittleness, and glossiness below estimated each obtained ink jet record form. In addition, ink absorptivity used ink jet printer MJ[ by Seiko Epson, Inc. ]-900C.

[0098] (1) Ink absorptivity : homogeneity was made to breathe out and it recorded so that the amount of the maximum ink might become 40%, respectively, and 20 red-reflex concentration of the solid section was measured using the microdensitometer (aperture =200micrometerphi), and the value of yellow and cyanogen broken by average reflection density in quest of the standard deviation of the variation in the concentration was calculated.

[0099] When ink absorptivity is good, the value of non-Lycium chinense becomes [ nonuniformity ] small at an image, but if ink absorptivity falls, this each other liquid ink drops will cause beading mutually in the record paper, it will become nonuniformity, and this value will increase.

[0100] (2) Coat brittleness : after saving each ink jet record form in the condition of having made it the shape of a cylinder with a diameter of 60mm one whole day and night so that a printing side may become outside at 25 degrees C and 20% of relative humidity, the surface crack condition was observed with the magnifier.

[0101]

O : — condition O: which does not have a crack with a magnifier, either — although a crack is partially seen with a magnifier, there is no crack, and a cracking crack is accepted with a magnifier, and, as for an image-quality top, a crack also looks at an image-quality top in almost uninfluential \*\*:viewing by x:viewing as which a bad influence is regarded — having — a (3) glossiness record stratification plane with the effect very large moreover of [ on image quality ] Gloss was measured

75 degrees using the deflection glossmeter (VGS-1001-DP) by Nippon Denshoku Industries Co., Ltd.

[0102] The obtained result is shown in Table 2.

[0103]

[Table 2]

記録用紙	インク吸収性	脆弱性	光沢
1 (比較例)	0.04	×	61%
2 (比較例)	0.04	×	61%
3 (本発明)	0.05	○	60%
4 (本発明)	0.06	○	58%
5 (比較例)	0.10	○	38%
6 (比較例)	0.04	×	60%
7 (本発明)	0.05	○	61%
8 (本発明)	0.06	○	59%
9 (比較例)	0.11	○	43%
10 (比較例)	0.05	×	46%
11 (比較例)	0.06	×	53%

記録用紙：インクジェット記録用紙

[0104] It turns out that 3, 4, 7, and 8 which are the ink jet record form of this invention can improve the brittleness of a coat greatly from the result of Table 2, without reducing ink absorptivity, and there is moreover almost no fall of gloss.

[0105] On the other hand, ink jet record form whose addition of an oil droplet is below this invention - 2 and 6 are an ink jet record form whose addition of an oil droplet it crocodiles, there is almost no amelioration effectiveness, and is more than this invention on the other hand. - The rate of absorption of ink falls and an glossy fall is also large at 5 and 9.

[0106] On the other hand, when the hydrophobic organic compound with which the melting point exceeds 40 degrees C is used, it crocodiles and there is no amelioration effectiveness.

[0107] Ink jet record form which added polymeric latex in coating liquid in the ink jet record form of example 2 example 1 as shown in Table 3 - 21-28 were produced like the ink jet record form -1.

[0108] It was similarly estimated as the example 1 and the result shown in Table 4 was obtained.

[0109]

[Table 3]

記録用紙	添加剤 (Tg)	液滴径	添加量
2 1 (本発明)	ET/VA (Tg<20°C)	0.10 μm	10%
2 2 (本発明)	"	"	30%
2 3 (比較例)	"	"	60%
2 4 (本発明)	ST/BA/HEMA (Tg<20°C)	0.09 μm	10%
2 5 (本発明)	"	"	30%
2 6 (比較例)	"	"	60%
2 7 (比較例)	ST (Tg=100°C)	0.12 μm	20%
2 8 (比較例)	BMA (Tg=57°C)	0.08 μm	20%

ET/VA : エチレン/酢酸ビニル共重合ラテックス (10/90)

ST/BA/HEMA : スチレン/ブチルアクリレート/ヒドロキシルエチルメク  
リレート共重合ラテックス (20/70/10)

ST : ポリスチレンラテックス

BMA : ポリブチルアクリレート

記録用紙：インクジェット記録用紙

[0110]

[Table 4]

記録用紙	インク吸収性	脆弱性	光沢
2 1 (本発明)	0.05	○	62%
2 2 (本発明)	0.07	○	64%
2 3 (比較例)	0.13	◎	48%
2 4 (本発明)	0.05	○	59%
2 5 (本発明)	0.06	○	57%
2 6 (比較例)	0.11	○	45%
2 7 (比較例)	0.07	×	51%
2 8 (比較例)	0.08	△	42%

記録用紙：インクジェット記録用紙

[0111] Ink jet record form which glass transition temperature is 40 degrees C or less, and was contained from the result of Table 4 five to 50% of the weight to the silica even if it was the case where polymeric latex was used as an oil droplet – It turns out that a crack is improved, without 21, 22, 24, and 25 degrading ink absorptivity and glossiness. When it is used exceeding 50 % of the weight, although the crack is good, ink absorptivity and glossiness fall.

[0112] Moreover, a crack is not improved when the polymeric latex to which glass transition temperature exceeded 40 degrees C is used.

[0113] The photograph form base material which covered 3100g of examples/, and stencil paper both sides of m2 with polyethylene (it is 7% of the weight of anatase mold titanium oxide content in the polyethylene layer by the side of 140 micrometers in thickness, and an ink jet record stratification plane.) Spreading desiccation was carried out so that humid thickness might be set to 150 micrometers in the following [coating liquid –2] at the field side for ink jet record in [ having the layer which contains alkali treatment gelatin 4.2 g/m2 and a hardening agent as a back layer in the rear-face side by the side of an ink jet record stratification plane ], and the layer which has an opening was painted on the base material.

[0114]

[Coating liquid –1]

Pure water 980ml Gaseous-phase method particle silica whose mean particle diameter is 0.007 micrometers 48.0g Average degree of polymerization is polyvinyl alcohol of 3500. 10.8g (whenever [ PVA3500 and saponification ] 94%)

Surfactant –1 (AS-1) Spreading desiccation of the [coating liquid –3] of the following presentations on 1.2g, next this spreading layer was carried out so that humid thickness might turn to 8 micrometers, and the ink jet record form –31 was obtained.

[0115]

[Coating liquid –2]

Pure water Phenylcarbamoyl-ized gelatin 800ml (the rate of an amino-group blockade = 88%) 40g Polyvinyl pyrrolidone (K-90) 25g Polyethylene oxide (average molecular weight = about 150,000) 12g Surfactant –2 (AS-2) 0.7g Hardening agent –1 2.1g AS-2 : Sulfo succinic-acid-diethyl ester-sodium salt a hardening agent –1:1 and a 5-diglycidyl-3-hydroxy pentane — next, set in the ink jet record form –31 It is an ink jet record form as well as the ink jet record form –31 using the [coating liquid –2] which added LP distribution object as shown in Table 5. – 32-34 were produced.

[0116] In addition, at the time of addition of LP distribution object, the amount of pure water was adjusted so that the total amount of coating liquid might become fixed.

[0117] Moreover, used LP distribution object was a 8-% of the weight distribution object of a liquid paraffin, and the particle size of the diameter of a drop was 0.13 micrometers about.

[0118]

[Table 5]

記録用紙	分散物	油滴比率(対シリカ)
3 1 (比較例)	–	0%
3 2 (本発明)	LP 分散液 60ml	10%
3 3 (本発明)	〃 250ml	42%
3 4 (比較例)	〃 600ml	100%

記録用紙：インクジェット記録用紙

[0119] The obtained ink jet record form was evaluated like the example 1. A result is shown in Table 6.

[0120]

[Table 6]

記録用紙	インク吸収性	脆弱性	光沢
3 1 (比較例)	0.10	×	74%
3 2 (本発明)	0.12	△	72%
3 3 (本発明)	0.13	○	68%
3 4 (比較例)	0.19	○	48%

記録用紙：インクジェット記録用紙

[0121] When the swelling layer which makes the gelatin of the maximum upper layer a subject is prepared from the result shown in Table 6, although ink absorptivity falls to the whole, glossiness improves.

[0122] Also in this, it is the ink jet record form of this invention. – 32 and 33 have comparatively few ink absorptivity and glossy falls, and, moreover, a crack is improved greatly.

[0123] On the other hand, the ink absorptivity and the glossiness of what has the ink jet record form –34 good [ a crack ] which added the liquid paraffin 100% of the weight to the silica are falling greatly.

[0124] Except having changed [coating liquid –2] into the following [coating liquid–2a] in example 4 example 3, the DIDP dispersion liquid (the particle size of 10-% of the weight content and a drop is about 0.23 micrometers about di-isodecyl phthalate) shown in Table 7 like an example 3 are added, and it is an ink jet record form. – It is the ink jet record form of a configuration like 31–34. – 41–44 were produced and it was similarly estimated as the example 3. A result is shown in Table 8.

[0125]

[Coating liquid–2a]

Pure water 920ml Particle calcium carbonate (mean particle diameter = about 0.03 micrometers)  
120g Polyvinyl alcohol of average degree of polymerization 1700 6.2g (whenever [ saponification ] 90%)

Surfactant –1 1.0g [0126]

[Table 7]

記録用紙	分散物	炭酸カルシウムに対する比率
4 1 (比較例)	—	0%
4 2 (本発明)	D I 分散液 60ml	5.0%
4 3 (本発明)	〃 250ml	20.8%
4 4 (比較例)	〃 650ml	54.2%

記録用紙：インクジェット記録用紙

[0127]

[Table 8]

記録用紙	インク吸収性	脆弱性	光沢
4 1 (比較例)	0.14	×	75%
4 2 (本発明)	0.14	△	74%
4 3 (本発明)	0.15	○	70%
4 4 (比較例)	0.23	○	53%

記録用紙：インクジェット記録用紙

[0128] The result of Table 8 shows that the effectiveness as an example 3 that it is the same even when a particle calcium carbonate is used as a solid-state particle is acquired.

[0129] It is an ink jet record form as well as the ink jet record form –1 except having changed 8g polyvinyl alcohol (average degree of polymerization 3500) into the combination of high-polymer polyvinyl alcohol and low degree-of-polymerization polyvinyl alcohol in the ink jet record form –1 produced in the example 5 example 1, as shown in Table 9. – 51–61 were produced. (All of the amount of polyvinyl alcohol are the same.)

Among a table, it reaches high-polymer PVA and the low degree of polymerization PVA shows the

amount of high polymerization and the polyvinyl alcohol of a low degree of polymerization, respectively.

[0130]

[Table 9]

記録用紙	高重合度PVA			低重合度PVA			低重合度 比率(%)
	量 (g)	ケン化度 (%)	重合度	量 (g)	ケン化度 (%)	重合度	
1(比較例)	8.0	88	3500	0.0	—	—	0%
5.1(本発明)	7.9	88	3500	0.1	88	300	1.3%
5.2(本発明)	7.7	88	3500	0.3	88	300	3.9%
5.3(本発明)	7.0	88	3500	1.0	88	300	14.3%
5.4(本発明)	6.0	88	3500	2.0	88	300	33.3%
5.5(本発明)	7.7	88	3500	0.3	88	500	3.9%
5.6(本発明)	7.7	88	3500	0.3	88	700	3.9%
5.7(比較例)	7.7	88	3500	0.3	88	1100	3.9%
5.8(本発明)	7.7	88	2500	0.3	88	300	3.9%
5.9(比較例)	7.7	88	1750	0.3	88	300	3.9%
6.0(本発明)	7.7	98	3500	0.3	82	300	3.9%
6.1(本発明)	7.5	88	3500	0.3	88	300	4.0%

記録用紙：インクジェット記録用紙

[0131]

[Table 10]

記録用紙	インク吸収性	脆弱性		光沢
		保存前	加熱保存後	
1(比較例)	0.04	×	×	61%
5.1(本発明)	0.04	○	△	64%
5.2(本発明)	0.04	○	○	69%
5.3(本発明)	0.04	○	○	68%
5.4(本発明)	0.04	○	△	65%
5.5(本発明)	0.05	○	○	61%
5.6(本発明)	0.04	○	△	59%
5.7(比較例)	0.04	×	×	59%
5.8(本発明)	0.04	○	○	58%
5.9(比較例)	0.05	×	×	41%
6.0(本発明)	0.05	○	○	66%
6.1(本発明)	0.05	○	○	65%

記録用紙：インクジェット記録用紙

[0132] From the result of Table 10, average degree of polymerization is improved as compared with the sample -1 which the ink jet record form (51, 52, 53, 54, 55, 56, 58, 60, 61) which used together 1000 or less polyvinyl alcohol of a low degree of polymerization with 2000 or more average degree of polymerization high-polymer polyvinyl alcohol is before and after heat-treatment, and the brittleness of a coat does not use together. Especially, the degree of polymerization of low degree-of-polymerization polyvinyl alcohol is 500 or less, and it turns out that the sample (52, 53, 55, 58, 60, 61) whose ratio to high polymerization is 2 - 20% has good brittleness especially.

[0133] Moreover, the average degree of polymerization of high-polymer polyvinyl alcohol is 3000 or more, and it turns out that, as for especially the ink jet record form (60 51-54, 61) of 400 or less this invention, the average degree of polymerization of low degree-of-polymerization polyvinyl alcohol is excellent in glossiness.

[0134] It is an ink jet record form as well as the ink jet record form -31 except having changed into the combination of high-polymer polyvinyl alcohol and low degree-of-polymerization polyvinyl alcohol the 10.8g polyvinyl alcohol (average degree of polymerization 3500) used with coating liquid -1 in the ink jet record form -31 produced in the example 6 example 3, as shown in Table 11. - 71-78 were produced (all of the amount of polyvinyl alcohol are the same.).

[0135]

[Table 11]

記録用紙	高重合度PVA			低重合度PVA			低重合度比率(%)
	量(g)	ケン化度(%)	重合度	量(g)	ケン化度(%)	重合度	
3 1(比較例)	10.8	88	3500	0.0	—	—	0%
7 1(本発明)	10.3	88	3500	0.5	88	300	4.8%
7 2(本発明)	9.3	88	3500	1.5	88	300	16.1%
7 3(本発明)	8.8	88	3500	2.0	88	300	22.7%
7 4(本発明)	8.3	88	3500	2.5	88	300	30.1%
7 5(本発明)	10.3	88	3500	0.5	88	700	4.8%
7 6(比較例)	10.3	88	3500	0.5	88	1100	4.8%
7 7(本発明)	10.3	88	2500	0.5	88	300	4.8%
7 8(比較例)	10.3	88	1750	0.5	88	300	4.8%

記録用紙：インクジェット記録用紙

[0136] The obtained sample was similarly estimated as the example -5, and the result shown in Table 12 was obtained.

[0137]

[Table 12]

記録用紙	インク吸収性	脆弱性		光沢
		保存前	加熱保存後	
3 1(比較例)	0.10	×	×	74%
7 1(本発明)	0.11	○	○	75%
7 2(本発明)	0.10	○	○	73%
7 3(本発明)	0.10	○	△	69%
7 4(本発明)	0.11	△	△	65%
7 5(本発明)	0.11	○	△	70%
7 6(比較例)	0.10	×	×	67%
7 7(本発明)	0.11	○	△	71%
7 8(比較例)	0.10	×	×	50%

記録用紙：インクジェット記録用紙

[0138] The result of Table 12 shows that the brittle amelioration effectiveness which is the effectiveness of this invention even if it is the case where the thin swelling layer which makes gelatin a subject is prepared in the maximum upper layer, and high glossiness are acquired in the ink jet record form (71 to 75-77) of this invention.

[0139] In the ink jet record form -7 produced in the example 7 example 1, 8g average degree of polymerization produced the ink jet record form -80 as well as the ink jet record form -7, except that the polyvinyl alcohol of 3500 and 0.5g average degree of polymerization changed [ 7.5g average degree of polymerization ] the polyvinyl alcohol of 3500 into concomitant use of the polyvinyl alcohol of 300. When it was similarly estimated as the example 1, it is ink absorptivity:0.04 brittleness: O glossiness: The result of 66% was obtained. This shows that brittleness is improved further further, if use of use of \*\*\*\*, low degree-of-polymerization polyvinyl alcohol, and high-polymer polyvinyl alcohol is used together.

[0140]

[Effect of the Invention] As the example proved, the ink jet record form by this invention has the high ink absorptivity containing the solid-state particle distributed in the hydrophilic binder, even if it is the case where it saves under damp, the brittleness of a coat does not fall, but it has the effectiveness which high-definition ink jet record was possible for, and was excellent.

[Translation done.]

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**TECHNICAL FIELD**

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**[Field of the Invention]** This invention relates to the ink jet record form which has improved especially ink absorptivity about the ink jet record form which records using water color ink.

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## PRIOR ART

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[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] As an ink jet record form used by this ink jet recording method, also when a printing dot laps [ that a color tone is brightly skillful and absorption of ink ] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [ the concentration of a printing dot is high, and ] beyond the need, and it is required that the circumference should be smooth and should not fade etc.

[0004] Since it becomes nonuniformity, and the color of each other in the border area of a color which a drop causes a HAJIKI phenomenon on an ink jet record form, and is different spreads and it is easy to reduce image quality greatly in case the liquid ink drop of two or more colors laps and is recorded, when especially ink rate of absorption is slow, it is required to give ink absorptivity high as an ink jet record form.

[0005] In order to solve these problems, very many techniques are proposed from the former.

[0006] As the pigment in \*\*\*\*-ed indicated by the ink jet record form which carried out humidity of the coating for surface treatment to the low size stencil paper indicated by JP,52-53012,A, the ink jet record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, and JP,56-157,A The ink jet record form containing non-colloid silica powder, the ink jet record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The ink jet record form which has two hole distribution peaks indicated by JP,58-110287,A, The ink jet record form which consists of a vertical two-layer porous layer indicated by JP,62-111782,A, The ink jet record form which has the indeterminate form crack indicated by JP,59-68292,A, 59-123696, the 60-18383 official report, etc., The ink jet record form which has the impalpable powder layer indicated by JP,61-135786,A, 61-148092, the 62-149475 official report, etc., JP,63-252779,A, JP,1-108083,A, 2-136279, The ink jet record form containing the pigment which has the specific physical-properties value indicated by 3-65376, 3-27976, etc., or a particle silica, JP,57-14091,A, 60-219083, 60-210984, 61-20797, 61-188183, JP,5-278324,A, 6-92011, 6-183134, 7-137431, The ink jet record form containing particle silicas, such as a colloid silica indicated by 7-276789 etc., And JP,2-276671,A, a 3-67684 official report, 3-215082, A large number are known for the ink jet record form containing the hydrated alumina particle indicated by 3-251488, 4-67986, 4-263983, the 5-16517 official report, etc.

[0007] Especially, an ink absorbing layer can absorb ink, or when it is the layer (henceforth an opening layer) which has many openings for holding, ink absorptivity is good, there are few blots of the boundary section, and a quality image can be recorded.

[0008] And since that capacity may change under high-humidity/temperature especially while this opening saves, it is desirable that a solid-state particle from which an opening does not change into an opening layer is included.

[0009] To make a solid-state particle contain and make an opening form in an opening layer, it is required in order for making a hydrophilic binder contain to make a stable coat form. However, if there are too many additions to the solid-state particle of a hydrophilic binder, the opening made to form between the solid-state particle itself or a solid-state particle will be taken up, or there will be a problem of this hydrophilic binder itself swelling in early stages of ink absorption at the time of ink absorption, plugging up an opening layer, and reducing ink absorptivity, and that amount used will be limited.

[0010] According to examination of this invention persons, the ratio of the addition of the hydrophilic binder to a solid-state particle is understood that it is required to increase 2 to 200 times in general at a weight ratio.

[0011] It has the fault containing the solid-state particle of such a high ratio that the brittleness of a coat is inferior, carrying out layer measles, and when saved especially under damp, a detailed crack condition is generated on the front face of an ink absorption layer. When ink jet record is performed in such an ink jet record form, ink will spread along with this cracked line, and image quality will be reduced remarkably.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] As the example proved, the ink jet record form by this invention has the high ink absorptivity containing the solid-state particle distributed in the hydrophilic binder, even if it is the case where it saves under damp, the brittleness of a coat does not fall, but it has the effectiveness which high-definition ink jet record was possible for, and was excellent.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned actual condition, and the purpose of this invention is to offer [ have the high ink absorptivity containing the solid-state particle distributed in the hydrophilic binder, for the brittleness of a coat not to fall, even if it is the case where it saves under damp, but ] the ink jet record form in which high-definition ink jet record is possible.

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MEANS

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[Means for Solving the Problem] The above-mentioned purpose of this invention is attained by the following configurations.

[0014] 1. Ink jet record form with which layer containing this solid-state particle is characterized by 1000 or less polyvinyl alcohol and average degree of polymerization containing [ average degree of polymerization ] 2000 or more polyvinyl alcohol in ink jet record form with which it has at least one-layer ink absorption layer containing solid-state particle and polyvinyl alcohol, and at least one layer of this ink absorption layer contains solid-state particle two to 200 times by weight ratio to total amount of polyvinyl alcohol on base material.

[0015] 2. Ink jet record form given in said 1 characterized by said solid-state particle being solid-state particle chosen from silica whose mean particle diameter of primary particle is 7-80nm, respectively, calcium carbonate, alumina, hydrated alumina, or magnesium silicate.

[0016] 3. Ink jet record form given in said 1 characterized by said solid-state particle being silica compounded by gaseous-phase method mean particle diameter of primary particle is 7-30nm.

[0017] 4. Ink jet record form given in said any 1 term of 1-3 to which said average degree of polymerization is characterized by 1000 or less amount of polyvinyl alcohol being [ average degree of polymerization ] 1 - 30 % of the weight in weight ratio to 2000 or more polyvinyl alcohol.

[0018] 5. It Has at Least One Layer of Ink Absorption Layers Which Contain Solid-state Particle and Polyvinyl Alcohol at Least as a Hydrophilic Binder on Base Material. It is the ink jet record form whose weight ratio of the solid-state particle to the hydrophilic binder of at least one layer of this ink absorption layer is two to 200 times. The ink jet record form with which the hydrophobic organic compound or glass transition temperature of 40 degrees C or less is characterized by this ink absorption layer containing the oil droplet as which the melting point is chosen from polymeric latex 40 degrees C or less five to 50% of the weight to a solid-state particle.

[0019] 6. Ink jet record form given in said 5 characterized by mean diameter of said oil droplet being 0.05-0.5 micrometers.

[0020] 7. Said 5 characterized by said solid-state particle being solid-state particle chosen from silica whose mean particle diameter of primary particle is 7-80nm, respectively, calcium carbonate, alumina, hydrated alumina, or magnesium silicate, or ink jet record form given in 6.

[0021] 8. Said 5 characterized by said solid-state particle being silica compounded by gaseous-phase method mean particle diameter of primary particle is 7-30nm, or ink jet record form given in 6.

[0022] Hereafter, this invention is explained to a detail.

[0023] Although the solid-state particle which the ink jet record form of this invention contains can use a well-known solid-state particle conventionally in an ink jet record form, its non-subtlety particle is desirable.

[0024] it is used for this purpose — well-known, if a non-subtlety particle is carried out at an ink jet — for example Precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, Clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, Zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, White inorganic pigments, such as the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a

magnesium hydroxide, etc. can be used.

[0025] Such a non-subtlety particle may be added in the condition of being used into a binder after homogeneity has distributed having also formed secondary floc with the primary particle, and having distributed in the binder.

[0026] On the other hand as an example of an organic particle, polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, or melamine resin is mentioned.

[0027] It is desirable to use an inorganic solid-state particle from the point that an opening layer with comparatively high voidage is obtained in this invention. It is desirable that the point that high glossiness and high image concentration are easy to be obtained especially to a solid-state particle is a solid-state particle chosen from a silica, a calcium carbonate, an alumina, hydrated alumina, or a magnesium silicate.

[0028] As a silica system particle preferably used in the ink jet record form of this invention, various kinds of well-known silica system particles can be conventionally used by the ink jet.

[0029] For example, the synthetic silica compounded by wet or the gaseous-phase method, colloidal silica, and the silica of the configuration of the porosity silica arbitration which a primary particle condenses and forms the secondary particle can be used. As such an example, for example, the synthetic amorphous silica indicated by JP,55-51583,A, 56-148583, etc., For example, the silica ultrafine particle compounded by the gaseous-phase method indicated by JP,60-204390,A, The synthetic indeterminate form silica containing the fluorine indicated by JP,60-222282,A, The synthetic indeterminate form silica in which surface treatment was carried out by the silane coupling agent indicated by JP,60-224580,A and 62-178384, For example, the spherical silica indicated by JP,62-183382,A and 63-104878, The synthetic silica particle whose Na<sub>2</sub>O content indicated by JP,63-317381,A is 0.5 % of the weight or more, The specific surface area indicated by JP,1-115677,A The synthetic silica particle more than 100m<sup>2</sup>/g, The synthetic silica particle which was indicated by JP,62-286787,A and by which alumina surface treatment was carried out, The synthetic silica particle by which surface treatment was carried out with salts, such as calcium, Mg, or Ba indicated by JP,1-259982,A, The colloidal silica oil absorption was indicated to be by a 180ml [ /g ] or more composition silica particle and JP,57-14091,A, The cationic colloidal silica indicated by JP,60-219084,A, JP,6-92011,A, 6-297830, and 7-81214, And the colloidal silica which connected in the shape of [ which was indicated by JP,5-278324,A and 7-81214 ] a rosary, or branched can be mentioned.

[0030] However, in order to obtain high glossiness and the high amount of openings, it is desirable to use the ultrafine particle silica whose mean particle diameter is 7-80nm. This silica particle may be the object which cation conversion could be carried out in the front face, and was processed by aluminum, calcium, Mg, Ba, etc.

[0031] As a calcium carbonate preferably used in the ink jet record form of this invention For example, JP,57-12486,A, 57-129778, 58-55283, The precipitated calcium carbonate which has specific surface area in the specification indicated by 61-20792, The needle pillar-shaped calcium carbonate indicated by JP,63-57277,A and JP,4-250091,A, The calcium-carbonate particle which the specific needlelike primary particle indicated by JP,3-251487,A condensed, and formed the secondary particle, the needle which has the specific oil absorption indicated by JP,4-250091,A and 4-260092 — a pillar-shaped prismatic crystal Argo night calcium carbonate, the spherical precipitated calcium carbonate indicated by JP,7-40648,A are mentioned.

[0032] In this case, since high glossiness and the high amount of openings can be obtained, it is desirable to use the calcium-carbonate particle whose particle size is about 7-80nm.

[0033] Tabular is desirable although the magnesium silicates preferably used by this invention may be an indeterminate form particle, a globular shape, and tabular any. The mean particle diameter of a tabular magnesium silicate is expressed with the diameter when converting this into a circle in quest of a tabular average projected area, and its 7-80nm particle is desirable.

[0034] The alumina or hydrated alumina preferably used by this invention may be crystallinity, or may be amorphous, and a configuration can use the object of the configuration of arbitration, such as an indeterminate form particle, a spherical particle, and a needlelike particle.

[0035] The mean particle diameter of various kinds of above-mentioned inorganic solid-state

particles measures the average projected area when photoing it with an electron microscope, and expresses the diameter when converting this into a circle.

[0036] As for especially the above-mentioned solid-state particle preferably used by this invention, it is desirable that it is that whose mean particle diameter of a primary particle is 7-80nm.

[0037] When primary particle diameter is less than 7nm, handling nature is difficult, and the fall of gloss tends to become remarkable in exceeding 80nm.

[0038] The above-mentioned solid-state particle content layer needs to contain a hydrophilic binder in respect of coat formation in the ink jet record form of this invention.

[0039] As a hydrophilic binder generally used for an ink jet record form Gelatin or a gelatin derivative, a polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), A pullulan, polyvinyl alcohol, or its derivative (about 20,000 or more have desirable average molecular weight), A polyethylene glycol (100,000 or more have a desirable mean molecular weight), a carboxymethyl cellulose, Hydroxyethyl cellulose, a dextran, a dextrin, polyacrylic acid, and its salt, An agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, A polyalkylene oxide system copolymerization nature polymer given in locust bean gum, an alginic acid, gum arabic, a pullulan, JP,7-195826,A, and 7-9757, Although polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has a water-soluble polyvinyl butyral, or a carboxyl group and a sulfonic group given in JP,62-245260,A, etc. are known, it sets to this invention. It is required in the viewpoint of smeariness prevention high ink absorptivity and high glossiness, and control of further curl and under highly humid to contain polyvinyl alcohol at least.

[0040] In polyvinyl alcohol here, the polyvinyl alcohol by which cation denaturation was carried out in addition to the polyvinyl alcohol usually said, such as a partial saponification object or a full saponification object of polyvinyl acetate, is also contained.

[0041] As for whenever [ saponification / of the above-mentioned polyvinyl acetate ], 70 - 99% of thing is preferably used by this invention 60 to 100%.

[0042] Moreover, the desirable polyvinyl alcohol by which cation denaturation was carried out is obtained by saponifying the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical.

[0043] As an ethylenic unsaturated monomer which has a cationic radical For example, TORIMECHIRU-(2-acrylamide -2, 2-dimethyl ethyl) ammoniumchloride, TORIMECHIRU-(3-acrylamide -3, 3-dimethyl propyl) ammoniumchloride, N-vinyl imidazole, N-vinyl-2-methylimidazole, N-(3-dimethylaminopropyl) methacrylamide, Hydroxyl ethyl trimethylammonium chloride, TORIMECHIRU-( methacrylamide propyl) ammoniumchloride, N-(1 and 1-dimethyl-3-dimethylaminopropyl) acrylamide, etc. are mentioned.

[0044] 0.1-10-mol% of the ratio of the cation denaturation radical content monomer of cation denaturation polyvinyl alcohol is desirable to vinyl acetate, and is 0.2-5-mol % more preferably. Moreover, whenever [ 60 - 100% of ], whenever [ saponification / of cation denaturation polyvinyl alcohol ] is desirable, and it is 70 - 99% more preferably.

[0045] In the ink jet record form of this invention, the ratio to the hydrophilic binder of the solid-state particle which forms an opening layer is a weight ratio, and needs to be two to 200 times. It becomes, and a hydrophilic binder swells at the time of ink absorption that it is easy to produce the problem of everything accompanying thickness being too thick at the time under of 2 double in order for the rate of a void ratio formed to absorb the amount of the maximum ink completely small, the ink rate of absorption of an opening layer is reduced, and the image quality acquired is reduced.

[0046] On the other hand, in exceeding 200 times, it it adopts the below-mentioned various means, the brittleness of a coat deteriorates greatly and high-definition ink jet record becomes impossible.

[0047] It is 2.5 to 100 times the desirable ratio of this, and is especially 3 to 50 times the desirable ratio of this.

[0048] Moreover, as a solid-state particle, when a desirable gaseous-phase method silica is used especially, desirable ratios are 3-20.

[0049] In order to improve the coat brittleness accompanying this, since the opening layer of the

ink jet record form of this invention contains the solid-state particle of a high ratio especially to a hydrophilic binder like the above \*\* This solid-state particle content layer [ whether 1000 or less polyvinyl alcohol and average degree of polymerization contain / average degree of polymerization / 2000 or more polyvinyl alcohol and ] Or that thing [ that any one is filled at least ] in which \*\* solid-state particle content layer contains an oil droplet five to 50% of the weight to a solid-state particle is required.

[0050] In the above and \*\*, it is desirable to use more nearly high-polymer polyvinyl alcohol for formation of the stable coat which cannot produce a crack easily, and a coat with good extent which is that average degree of polymerization uses 2000 or more polyvinyl alcohol independently from this viewpoint is obtained. Conversely, especially when only the polyvinyl alcohol of low molecular weight is used, in the coat containing many solid-state particles, it is easy to produce a crack in the desiccation process after spreading.

[0051] However, when a crack with a coat minute when average degree of polymerization uses only 2000 or more polyvinyl alcohol is not lost completely and it saves under an elevated temperature after spreading desiccation, the brittleness of a coat falls, and it becomes easy to produce a crack in a coat especially under low humidity conditions.

[0052] this invention persons find out that this problem is improved because average degree of polymerization uses together 1000 or less low degree-of-polymerization polyvinyl alcohol to the high polyvinyl alcohol of average degree of polymerization, and result it in the 1st this invention.

[0053] 3000 or more things of average degree of polymerization are [ average degree of polymerization ] desirable also especially of the 2000 or more polyvinyl alcohol. Since the liquid of the concentration which the solubility of polyvinyl alcohol falls and is made into the purpose becomes impossible easily as it generally high-polymerization-izes although the upper limit of average degree of polymerization is not limited from the point of brittle amelioration of a coat, as for average degree of polymerization, especially generally, 4000 or less are [ 5000 or less ] desirable.

[0054] As for average degree of polymerization, 400 or less are [ especially a desirable thing / 500 or less ] the most desirable [ average degree of polymerization ] on the other hand among 1000 or less polyvinyl alcohol.

[0055] Although especially the minimum of average degree of polymerization is not limited, it is usually 200 or more.

[0056] It is desirable that the amount of 1000 or less polyvinyl alcohol is [ average degree of polymerization ] 1 – 30% in a weight ratio to 2000 or more polyvinyl alcohol for average degree of polymerization. If the effectiveness of this invention becomes that it is hard to be obtained substantially and it exceeds 30% in being less than 1%, the plasticity of the coat after spreading desiccation becomes easy to get worse, and especially crack formation will increase or it will become easy for an adhesive property with a base material to fall. Especially the desirable range is 2 – 20%.

[0057] In the above-mentioned \*\*, it is roughly divided into two kinds of things as an oil droplet which an ink absorption layer contains.

[0058] The 1st [ the ] is the case where the melting point is the oil droplet in which said oil droplet has a hydrophobic organic compound 40 degrees C or less, and the 2nd thing is the case where said oil droplet is [ glass transition temperature ] polymeric latex 40 degrees C or less.

[0059] solubility [ usually as opposed to / in the oil droplet of the 1st type / water at a room temperature ] — less than [ 0.1% % of the weight ] — it is 0.01 or less % of the weight especially preferably, and the melting point is a hydrophobic organic compound 40 degrees C or less.

[0060] A hydrophobic polymer 40 degrees C or less is mentioned for the organic compound with which such a hydrophobic organic compound is known as a usual hydrophobic high-boiling point organic solvent, and the melting point.

[0061] as the above-mentioned hydrophobic organic compound — for example, phthalic ester (for example, dibutyl phthalate —) Phosphoric ester, such as dioctyl phthalate and di-isodecyl phthalate For example, (tricresyl phosphate, trioctylphosphate), etc., fatty acid ester (butyl stearate and a sebacic acid screw (2-ethylhexyl) —) Ethylene glycol distearate, glycero RUTORI butyrate, etc., Amides (N and N-diethyl lauryl amide, N, and N-diethyl-2-(2, 5-G t-amyl phenoxy)

butaneamide etc.) Ether (ethylene glycol dibutyl ether, DESHIRU ether, dibenzyl ether, etc.), a silicone oil, a liquid paraffin, etc. can be mentioned.

[0062] Moreover, the melting point is mentioned for Pori (2-ethylhexyl methacrylate), poly butyl methacrylate, copoly (butyl acrylate / hydroxyl ethyl methacrylate: 90/10), polyvinyl acetate, polyvinyl propionate, copoly (butyl acrylate / t-butyl acrylate / 2-ethylhexyl methacrylate / styrene: 60/20/10/10), etc. as a hydrophobic polymer 40 degrees C or less, for example.

[0063] The polymer whose average molecular weight is 5000 to about 100,000 as the above-mentioned hydrophobic polymer is used preferably. In the case of the polymer exceeding 100,000, it is hard coming to form the oil droplet of a particle by approaches, such as emulsification distribution mentioned later.

[0064] Emulsification distribution is preferably carried out under existence of a surfactant into a hydrophilic binder by the high-speed homogenizer, a high-pressure homogenizer, etc., and the above-mentioned hydrophobic organic compound is used. Under the present circumstances, it is desirable to carry out emulsification distribution under existence of low-boiling point organic solvents, such as ethyl acetate, propyl acetate, a methyl ethyl ketone, an acetone, N and N, and dimethylformamide, etc., although minuter \*\*\* is formed.

[0065] Moreover, although the organic compound to which the melting point exceeds 40 degrees C with other hydrophobic organic compounds (for example, an ultraviolet ray absorbent, a fluorescent brightener, an image stabilizer, etc.) at the time of this emulsification distribution can also be used together, it is desirable that 50% of the weight or more of the organic compound which forms \*\*\* preferably of the melting point is a compound 40 degrees C or less.

[0066] On the other hand, polymeric latex 40 degrees C or less is polymeric latex to which the polymerization of the 2nd glass transition temperature was carried out by the emulsion-polymerization method, for example, a styrene-butadiene copolymer latex, a polyacrylic ester system latex, a polymethacrylic-acid-ester system latex, a vinyl acetate system latex, an ethylene-vinyl acetate system latex, etc. are used preferably.

[0067] As an example of the above-mentioned polymer latex, for example, styrene / butadiene latex (7/3), a polyvinyl acetate latex, vinyl acetate / ethylene latex (9/1), vinyl acetate / ethyl methacrylate latex (5/5), a vinyl chloride/ethyl acrylate (3/2), an ethyl acrylate / methyl acrylate / HEMA (5/4/1), styrene / butyl acrylate / HEMA (1/6/3), a silicon latex, etc. can be mentioned. In the above, a \*\*\* ratio expresses a mole ratio and HEMA expresses hydroxyl ethyl methacrylate.

[0068] As for the mean particle diameter of various kinds of above-mentioned oil droplets, it is desirable that it is 0.05–0.5 micrometers. When the size of an oil droplet is 0.05 micrometers or less, it becomes, or it is easy to reduce the brittle amelioration effectiveness, and an oil droplet becomes being easy to become unstable. Moreover, when the size of an oil droplet exceeds 0.5 micrometers, it becomes easy for gloss to fall.

[0069] The above-mentioned oil droplet is required for using it five to 50% of the weight to the solid-state particle which an ink absorption layer contains to acquire the effectiveness of this invention.

[0070] When the ratio to the solid-state particle of an oil droplet is less than 5 % of the weight, the brittle amelioration effectiveness of a coat is inadequate, and in exceeding 50 % of the weight, the rate of a void ratio falls, ink absorption capacity falls or the fall of gloss tends to take place.

[0071] Especially the desirable amount used is 10 – 40 % of the weight.

[0072] The ink jet record form of this invention can also have the ink absorption layer containing a solid-state particle and a hydrophilic binder more than two-layer. In this case, although the class or ratio of a hydrophilic binder or a solid-state particle used for the ink absorption layer of these plurality is chosen as arbitration, at least one layer needs to use together two kinds of polyvinyl alcohol with which average degree of polymerization differs like this invention in this layer, or to add the oil droplet of this invention about the case where there is a layer from which the ratio of the solid-state particle to a hydrophilic binder has increased 2 to 200 times.

[0073] In order to pull out especially the effectiveness of this invention to the maximum extent, it is using together using the polyvinyl alcohol with which the above-mentioned average degree of polymerization's differs, and an oil droplet.

[0074] Although the ink jet record form of this invention has at least one-layer ink absorption layer

containing an above-mentioned solid-state particle and an above-mentioned hydrophilic binder, it can have a hydrophilic binder layer besides this solid-state particle content layer. Even if such a hydrophilic binder layer has the solid-state particle, it does not need to be, but when there is nothing, in case it is prepared in the side which is preferably separated from a base material from the solid-state particle content layer of this invention in an opening layer, it is desirable from the point of ink rate of absorption to make it 2 micrometers or less of desiccation thickness preferably set to 1.5 micrometers or less.

[0075] Various kinds of additives can be made to contain if needed in the layer of the arbitration by the side of the ink receptiveness layer of the ink jet record form of this invention.

[0076] For example, an ultraviolet ray absorbent given in JP,57-74193,A, a 57-87988 official report, and a 62-261476 official report, JP,57-74192,A, a 57-87989 official report, a 60-72785 official report, The fading inhibitor indicated by a 61-146591 official report, JP,1-95091,A, the 3-13376 official report, etc., An anion, a cation or the various surfactants of Nonion, JP,59-42993,A, The fluorescent brightener indicated by a 59-52689 official report, a 62-280069 official report, a 61-242871 official report, JP,4-219266,A, etc., Various well-known additives, such as lubricant, such as pH regulators, such as a sulfuric acid, a phosphoric acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, and a diethylene glycol, antiseptics, a thickener, a hardening agent, an antistatic agent, and a mat agent, can also be made to contain.

[0077] An inorganic or organic hardening agent can be used as a hardening agent, for example, chromium alum, formaldehyde, a glyoxal, an epoxy system compound, a vinyl sulfone system compound, an acryloyl system compound, s-triazine system compound, N-methylol system compound, a carbodiimide system compound, ethylene imino \*\*\*\*\* etc. can be used.

[0078] Although especially a limit does not have the amount of the spreading solid content by the side of the ink recording surface in the ink jet record form of this invention, 10 – 40 g/m<sup>2</sup> is desirable in general, and 20 – 30 g/m<sup>2</sup> is more desirable. In addition, from the field of prevention of the curl after record image formation, it is good to form as thinly as possible.

[0079] Into the configuration layer of the arbitration by the side of the ink recording surface of this invention, an alkali-metal weak acid salt the poly allylamine of publications, such as the poly cation polyelectrolyte of JP,56-84992,A, a basic latex polymer of JP,57-36692,A, JP,61-58788,A, and a 62-174184 official report, and given in JP,61-47290,A etc. can be used more than a kind as a deck-watertight-luminaire-ized agent of an image.

[0080] As a base material used for the ink jet record form of this invention, a thing well-known as a record form for ink jets can be used suitably conventionally.

[0081] The thing of a property which bears the radiant heat when being able to mention the film which consists of ingredients, such as polyester system resin, diacetate system resin, thoria TESETO system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, a plate, a glass plate, etc. as a transparency base material, for example, and being used as an OHP also in this is desirable, and especially polyethylene terephthalate is desirable. As thickness of such a transparent base material, about 10-200 micrometers is desirable.

[0082] Moreover, what carried out opacification processing of the sheet which consists of common paper, a synthetic paper, resin covering paper, cloth, wood, a metal, etc. as a base material used when there is no transparent need, for example, a plate, and the above-mentioned translucency base material with the well-known means can be mentioned. The so-called White pet which comes to add white pigments to the resin covering paper (the so-called RC paper) which has the polyolefin resin enveloping layer which added white pigments etc. at least to one side of a base paper as an opaque base material, and polyethylene terephthalate is desirable.

[0083] Especially the effectiveness of this invention has large effectiveness, when a base material is non-absorptivity, and transparency or an opaque polyethylene terephthalate base material, and the base material that covered both sides of stencil paper with hydrophobic resin, such as polyethylene, are used especially preferably.

[0084] It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of an ink absorbing layer for the purpose, such as to enlarge

bond strength of a base material and an ink television layer. Furthermore, the ink jet record form of this invention does not necessarily need to be colorlessness, and may be the colored record sheet.

[0085] In manufacturing the ink jet record form of this invention, the approach of applying each hydrophilic layer containing an ink receptiveness layer on a base material can be suitably chosen from a well-known approach, and can be performed.

[0086] As a spreading method, the extrusion coat method which uses a hopper the roll coating method, a rod bar coating method, the air-knife-coating method, a spray coating method, the curtain method of application, or given in a U.S. Pat. No. 2,681,294 official report is used preferably.

[0087] The water color ink said by this invention is the following coloring agent and a solvent object, and a record liquid that consists of other additives. Water soluble dye, such as direct dye well-known as a coloring agent at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used.

[0088] As a solvent of water color ink, water and water-soluble, various organic solvents For example, methyl alcohol, isopropyl alcohol, n-butyl alcohol, Alcohols, such as tert-butyl alcohol and isobutyl alcohol; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a ketone-alcohol; tetrahydrofuran, Ether, such as dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, Polyhydric alcohol, such as a diethylene glycol, a glycerol, and triethanolamine; Ethylene glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol methyl (or ethyl) ether and the triethylene glycol monobutyl ether, is mentioned.

[0089] Also in the water-soluble organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, and the triethylene glycol monobutyl ether etc. is desirable.

[0090] As an additive of other water color ink, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rusr-proofer, etc. are mentioned, for example.

[0091] In order that the wettability to an ink jet record form may make it good, in 20 degrees C, as for water-color-ink liquid, it is desirable that it is 25 – 60 dyne/cm, and it is desirable to have the surface tension of 30 – 50 dyne/cm within the limits more preferably.

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[Translation done.]

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EXAMPLE

[Example] Although an example is given and this invention is explained concretely, the embodiment of this invention is not limited to these.

[0093] It painted and dried and the ink jet record form -1 was produced so that humid thickness might be set to 190 micrometers to the printing paper base material for photographs (12% of the weight of anatase mold titanium oxide is contained in the polyethylene layer by the side of an ink absorption layer) which covered 1160g of examples/, and both sides of the stencil paper of m2 with polyethylene in the following coating liquid -1.

[0094] The slide hopper method performed spreading, and after spreading and after cooling at about 10 degrees C and drying for 1 minute by the wind of this temperature, by the 30 degrees C - 45 degrees C wind, it applied for 4 minutes and dried.

[0095]

Coating liquid -1 Pure water (ion exchange water) 950ml Ethanol 30ml 50ml Silica (gaseous-phase method [ primary / an average of / particle diameter is 13nm ] silica) 51g Polyvinyl alcohol 8g (whenever [ average-degree-of-polymerization =3500 and saponification ] = 88%)

Surfactant (AS-1) 0.1g AS-1: It is an ink jet record form as well as the ink jet record form -1 about the ink jet record form which added the organic compound of addition and a comparison for the hydrophobic organic compound of this invention in triisopropyl naphthalene sulfonic-acid sodium, next the ink jet record form -1 as shown in Table 1. - 2-11 were produced. However, with addition of an oil droplet, pure water adjusted the whole quantity of coating liquid so that it might become the same in each ink jet record form. Moreover, as a surfactant, under existence of AS-1, each above-mentioned hydrophobic compound carried out emulsification distribution, and added in polyvinyl alcohol.

[0096]

[Table 1]

記録用紙	添加剤 (融点)	油滴径	添加量
2 (比較例)	流動パラフィン ( $mp < 10^\circ\text{C}$ )	0.3 $\mu\text{m}$	3%
3 (本発明)	"	"	10%
4 (本発明)	"	"	30%
5 (比較例)	"	"	90%
6 (比較例)	D I D P ( $mp = -53^\circ\text{C}$ )	0.32 $\mu\text{m}$	3%
7 (本発明)	"	"	10%
8 (本発明)	"	"	30%
9 (比較例)	"	"	90%
10 (比較例)	固体パラフィン ( $mp = 60^\circ\text{C}$ )	0.36 $\mu\text{m}$	20%
11 (比較例)	D P P ( $mp = 74^\circ\text{C}$ )	0.28 $\mu\text{m}$	20%

D I D P : ジイソデシルフタレート

D P P : ジフェニルフタレート

表中、添加量はシリカに対する重量比で表した。

記録用紙 : インクジェット記録用紙

[0097] The approach of describing ink absorptivity, coat brittleness, and glossiness below estimated each obtained ink jet record form. In addition, ink absorptivity used ink jet printer MJ[ by Seiko

Epson, Inc. ]-900C.

[0098] (1) Ink absorptivity : homogeneity was made to breathe out and it recorded so that the amount of the maximum ink might become 40%, respectively, and 20 red-reflex concentration of the solid section was measured using the microdensitometer (aperture =200micrometerphi), and the value of yellow and cyanogen broken by average reflection density in quest of the standard deviation of the variation in the concentration was calculated.

[0099] When ink absorptivity is good, the value of non-Lycium chinense becomes [ nonuniformity ] small at an image, but if ink absorptivity falls, this each other liquid ink drops will cause beading mutually in the record paper, it will become nonuniformity, and this value will increase.

[0100] (2) Coat brittleness : after saving each ink jet record form in the condition of having made it the shape of a cylinder with a diameter of 60mm one whole day and night so that a printing side may become outside at 25 degrees C and 20% of relative humidity, the surface crack condition was observed with the magnifier.

[0101]

O : — condition O: which does not have a crack with a magnifier, either — although a crack is partially seen with a magnifier, there is no crack, and a cracking crack is accepted with a magnifier, and, as for an image-quality top, a crack also looks at an image-quality top in almost uninfluential \*\*:viewing by x:viewing as which a bad influence is regarded — having — a (3) glossiness record stratification plane with the effect very large moreover of [ on image quality ] Gloss was measured 75 degrees using the deflection glossmeter (VGS-1001-DP) by Nippon Denshoku Industries Co., Ltd.

[0102] The obtained result is shown in Table 2.

[0103]

[Table 2]

記録用紙	インク吸収性	脆弱性	光沢
1 (比較例)	0.04	×	61%
2 (比較例)	0.04	×	61%
3 (本発明)	0.05	○	60%
4 (本発明)	0.06	○	58%
5 (比較例)	0.10	○	38%
6 (比較例)	0.04	×	60%
7 (本発明)	0.05	○	61%
8 (本発明)	0.06	○	59%
9 (比較例)	0.11	○	43%
10 (比較例)	0.05	×	46%
11 (比較例)	0.06	×	53%

記録用紙：インクジェット記録用紙

[0104] It turns out that 3, 4, 7, and 8 which are the ink jet record form of this invention can improve the brittleness of a coat greatly from the result of Table 2, without reducing ink absorptivity, and there is moreover almost no fall of gloss.

[0105] On the other hand, ink jet record form whose addition of an oil droplet is below this invention - 2 and 6 are an ink jet record form whose addition of an oil droplet it crocodiles, there is almost no amelioration effectiveness, and is more than this invention on the other hand. - The rate of absorption of ink falls and an glossy fall is also large at 5 and 9.

[0106] On the other hand, when the hydrophobic organic compound with which the melting point exceeds 40 degrees C is used, it crocodiles and there is no amelioration effectiveness.

[0107] Ink jet record form which added polymeric latex in coating liquid in the ink jet record form of example 2 example 1 as shown in Table 3 - 21-28 were produced like the ink jet record form -1.

[0108] It was similarly estimated as the example 1 and the result shown in Table 4 was obtained.

[0109]

[Table 3]

記録用紙	添加剤 (Tg)	液滴径	添加量
2 1 (本発明)	ET/VA (Tg<20°C)	0.10 μm	10%
2 2 (本発明)	"	"	30%
2 3 (比較例)	"	"	60%
2 4 (本発明)	ST/BA/HEMA (Tg<20°C)	0.09 μm	10%
2 5 (本発明)	"	"	30%
2 6 (比較例)	"	"	60%
2 7 (比較例)	ST (Tg≈100°C)	0.12 μm	20%
2 8 (比較例)	BMA (Tg≈57°C)	0.08 μm	20%

ET/VA : エチレン/酢酸ビニル共重合ラテックス (10/90)

ST/BA/HEMA : スチレン/ブチルアクリレート/ヒドロキシルエチルメク  
リレート共重合ラテックス (20/70/10)

ST : ポリスチレンラテックス

BMA : ポリブチルアクリレート

記録用紙 : インクジェット記録用紙

[0110]

[Table 4]

記録用紙	インク吸収性	脆弱性	光沢
2 1 (本発明)	0.05	○	62%
2 2 (本発明)	0.07	○	64%
2 3 (比較例)	0.13	◎	48%
2 4 (本発明)	0.05	○	59%
2 5 (本発明)	0.06	○	57%
2 6 (比較例)	0.11	○	45%
2 7 (比較例)	0.07	×	51%
2 8 (比較例)	0.08	△	42%

記録用紙 : インクジェット記録用紙

[0111] Ink jet record form which glass transition temperature is 40 degrees C or less, and was contained from the result of Table 4 five to 50% of the weight to the silica even if it was the case where polymeric latex was used as an oil droplet - It turns out that a crack is improved, without 21, 22, 24, and 25 degrading ink absorptivity and glossiness. When it is used exceeding 50 % of the weight, although the crack is good, ink absorptivity and glossiness fall.

[0112] Moreover, a crack is not improved when the polymeric latex to which glass transition temperature exceeded 40 degrees C is used.

[0113] The photograph form base material which covered 3100g of examples/, and stencil paper both sides of m2 with polyethylene (it is 7% of the weight of anatase mold titanium oxide content in the polyethylene layer by the side of 140 micrometers in thickness, and an ink jet record stratification plane.) Spreading desiccation was carried out so that humid thickness might be set to 150 micrometers in the following [coating liquid -2] at the field side for ink jet record in [ having the layer which contains alkali treatment gelatin 4.2 g/m2 and a hardening agent as a back layer in the rear-face side by the side of an ink jet record stratification plane ], and the layer which has an opening was painted on the base material.

[0114]

[Coating liquid -1]

Pure water 980ml Gaseous-phase method particle silica whose mean particle diameter is 0.007 micrometers 48.0g Average degree of polymerization is polyvinyl alcohol of 3500. 10.8g (whenever [ PVA3500 and saponification ] 94%)

Surfactant -1 (AS-1) Spreading desiccation of the [coating liquid -3] of the following presentations on 1.2g, next this spreading layer was carried out so that humid thickness might turn to 8 micrometers, and the ink jet record form -31 was obtained.

[0115]

[Coating liquid -2]

Pure water Phenylcarbamoyl-ized gelatin 800ml (the rate of an amino-group blockade = 88%) 40g

Polyvinyl pyrrolidone (K-90) 25g Polyethylene oxide (average molecular weight = about 150,000) 12g Surfactant -2 (AS-2) 0.7g Hardening agent -1 2.1g AS-2 : Sulfo succinic-acid-diethyl ester-sodium salt a hardening agent -1:1 and a 5-diglycidyl-3-hydroxy pentane — next, set in the ink jet record form -31 It is an ink jet record form as well as the ink jet record form -31 using the [coating liquid -2] which added LP distribution object as shown in Table 5. - 32-34 were produced.

[0116] In addition, at the time of addition of LP distribution object, the amount of pure water was adjusted so that the total amount of coating liquid might become fixed.

[0117] Moreover, used LP distribution object was a 8-% of the weight distribution object of a liquid paraffin, and the particle size of the diameter of a drop was 0.13 micrometers about.

[0118]

[Table 5]

記録用紙	分散物	油滴比率(対シリカ)
3 1 (比較例)	—	0%
3 2 (本発明)	LP分散液 60ml	10%
3 3 (本発明)	〃 250ml	42%
3 4 (比較例)	〃 600ml	100%

記録用紙 : インクジェット記録用紙

[0119] The obtained ink jet record form was evaluated like the example 1. A result is shown in Table 6.

[0120]

[Table 6]

記録用紙	インク吸収性	脆弱性	光沢
3 1 (比較例)	0.10	×	74%
3 2 (本発明)	0.12	△	72%
3 3 (本発明)	0.13	○	68%
3 4 (比較例)	0.19	○	48%

記録用紙 : インクジェット記録用紙

[0121] When the swelling layer which makes the gelatin of the maximum upper layer a subject is prepared from the result shown in Table 6, although ink absorptivity falls to the whole, glossiness improves.

[0122] Also in this, it is the ink jet record form of this invention. - 32 and 33 have comparatively few ink absorptivity and glossy falls, and, moreover, a crack is improved greatly.

[0123] On the other hand, the ink absorptivity and the glossiness of what has the ink jet record form -34 good [ a crack ] which added the liquid paraffin 100% of the weight to the silica are falling greatly.

[0124] Except having changed [coating liquid -2] into the following [coating liquid-2a] in example 4 example 3, the DIDP dispersion liquid (the particle size of 10-% of the weight content and a drop is about 0.23 micrometers about di-isodecyl phthalate) shown in Table 7 like an example 3 are added, and it is an ink jet record form. - It is the ink jet record form of a configuration like 31-34. - 41-44 were produced and it was similarly estimated as the example 3. A result is shown in Table 8.

[0125]

[Coating liquid-2a]

Pure water 920ml Particle calcium carbonate (mean particle diameter = about 0.03 micrometers) 120g Polyvinyl alcohol of average degree of polymerization 1700 6.2g (whenever [ saponification ] 90%)

Surfactant -1 1.0g [0126]

[Table 7]

記録用紙	分散物	炭酸カルシウムに対する比率
4 1 (比較例)	—	0%
4 2 (本発明)	D I 分散液 60ml	5.0%
4 3 (本発明)	〃 250ml	20.8%
4 4 (比較例)	〃 650ml	54.2%

記録用紙 : インクジェット記録用紙

[0127]

[Table 8]

記録用紙	インク吸収性	脆弱性	光沢
4 1 (比較例)	0.14	×	75%
4 2 (本発明)	0.14	△	74%
4 3 (本発明)	0.15	○	70%
4 4 (比較例)	0.23	○	53%

記録用紙：インクジェット記録用紙

[0128] The result of Table 8 shows that the effectiveness as an example 3 that it is the same even when a particle calcium carbonate is used as a solid-state particle is acquired.

[0129] It is an ink jet record form as well as the ink jet record form -1 except having changed 8g polyvinyl alcohol (average degree of polymerization 3500) into the combination of high-polymer polyvinyl alcohol and low degree-of-polymerization polyvinyl alcohol in the ink jet record form -1 produced in the example 5 example 1, as shown in Table 9. - 51-61 were produced. (All of the amount of polyvinyl alcohol are the same.)

Among a table, it reaches high-polymer PVA and the low degree of polymerization PVA shows the amount of high polymerization and the polyvinyl alcohol of a low degree of polymerization, respectively.

[0130]

[Table 9]

記録用紙	高重合度PVA			低重合度PVA			低重合度 比率(%)
	量 (g)	ケン化度 (%)	重合度	量 (g)	ケン化度 (%)	重合度	
1 (比較例)	8.0	88	3500	0.0	—	—	0%
5 1 (本発明)	7.9	88	3500	0.1	88	300	1.3%
5 2 (本発明)	7.7	88	3500	0.3	88	300	3.9%
5 3 (本発明)	7.0	88	3500	1.0	88	300	14.3%
5 4 (本発明)	6.0	88	3500	2.0	88	300	33.3%
5 5 (本発明)	7.7	88	3500	0.3	88	500	3.9%
5 6 (本発明)	7.7	88	3500	0.3	88	700	3.9%
5 7 (比較例)	7.7	88	3500	0.3	88	1100	3.9%
5 8 (本発明)	7.7	88	2500	0.3	88	300	3.9%
5 9 (比較例)	7.7	88	1750	0.3	88	300	3.9%
6 0 (本発明)	7.7	98	3500	0.3	82	300	3.9%
6 1 (本発明)	7.5	88	3500	0.3	88	300	4.0%

記録用紙：インクジェット記録用紙

[0131]

[Table 10]

記録用紙	インク吸収性	脆弱性		光沢
		保存前	加熱保存後	
1 (比較例)	0.04	×	×	61%
5 1 (本発明)	0.04	○	△	64%
5 2 (本発明)	0.04	○	○	69%
5 3 (本発明)	0.04	○	○	68%
5 4 (本発明)	0.04	○	△	65%
5 5 (本発明)	0.05	○	○	61%
5 6 (本発明)	0.04	○	△	59%
5 7 (比較例)	0.04	×	×	59%
5 8 (本発明)	0.04	○	○	58%
5 9 (比較例)	0.05	×	×	41%
6 0 (本発明)	0.05	○	○	66%
6 1 (本発明)	0.05	○	○	65%

記録用紙：インクジェット記録用紙

[0132] From the result of Table 10, average degree of polymerization is improved as compared with the sample -1 which the ink jet record form (51, 52, 53, 54, 55, 56, 58, 60, 61) which used together 1000 or less polyvinyl alcohol of a low degree of polymerization with 2000 or more average degree of polymerization high-polymer polyvinyl alcohol is before and after heat-treatment, and the brittleness of a coat does not use together. Especially, the degree of polymerization of low degree-of-polymerization polyvinyl alcohol is 500 or less, and it turns out that the sample (52, 53, 55, 58, 60, 61) whose ratio to high polymerization is 2 - 20% has good brittleness especially.

[0133] Moreover, the average degree of polymerization of high-polymer polyvinyl alcohol is 3000 or more, and it turns out that, as for especially the ink jet record form (60 51-54, 61) of 400 or less this invention, the average degree of polymerization of low degree-of-polymerization polyvinyl alcohol is excellent in glossiness.

[0134] It is an ink jet record form as well as the ink jet record form -31 except having changed into the combination of high-polymer polyvinyl alcohol and low degree-of-polymerization polyvinyl alcohol the 10.8g polyvinyl alcohol (average degree of polymerization 3500) used with coating liquid -1 in the ink jet record form -31 produced in the example 6 example 3, as shown in Table 11. - 71-78 were produced (all of the amount of polyvinyl alcohol are the same.).

[0135]

[Table 11]

記録用紙	高重合度 P V A			低重合度 P V A			低重合度 比率(%)
	量 (g)	ケン化度 (%)	重合度	量 (g)	ケン化度 (%)	重合度	
3 1 (比較例)	10.8	88	3500	0.0	—	—	0%
7 1 (本発明)	10.3	88	3500	0.5	88	300	4.8%
7 2 (本発明)	9.3	88	3500	1.5	88	300	16.1%
7 3 (本発明)	8.8	88	3500	2.0	88	300	22.7%
7 4 (本発明)	8.3	88	3500	2.5	88	300	30.1%
7 5 (本発明)	10.3	88	3500	0.5	88	700	4.8%
7 6 (比較例)	10.3	88	3500	0.5	88	1100	4.8%
7 7 (本発明)	10.3	88	2500	0.5	88	300	4.8%
7 8 (比較例)	10.3	88	1750	0.5	88	300	4.8%

記録用紙：インクジェット記録用紙

[0136] The obtained sample was similarly estimated as the example -5, and the result shown in Table 12 was obtained.

[0137]

[Table 12]

記録用紙	インク吸収性	脆弱性		光沢
		保存前	加熱保存後	
3 1 (比較例)	0.10	×	×	74%
7 1 (本発明)	0.11	○	○	75%
7 2 (本発明)	0.10	○	○	73%
7 3 (本発明)	0.10	○	△	69%
7 4 (本発明)	0.11	△	△	65%
7 5 (本発明)	0.11	○	△	70%
7 6 (比較例)	0.10	×	×	67%
7 7 (本発明)	0.11	○	△	71%
7 8 (比較例)	0.10	×	×	50%

記録用紙：インクジェット記録用紙

[0138] The result of Table 12 shows that the brittle amelioration effectiveness which is the effectiveness of this invention even if it is the case where the thin swelling layer which makes gelatin a subject is prepared in the maximum upper layer, and high glossiness are acquired in the ink jet record form (71 to 75-77) of this invention.

[0139] In the ink jet record form -7 produced in the example 7 example 1, 8g average degree of

polymerization produced the ink jet record form -80 as well as the ink jet record form -7, except that the polyvinyl alcohol of 3500 and 0.5g average degree of polymerization changed [ 7.5g average degree of polymerization ] the polyvinyl alcohol of 3500 into concomitant use of the polyvinyl alcohol of 300. When it was similarly estimated as the example 1, it is ink absorptivity:0.04 brittleness. : O glossiness : The result of 66% was obtained. This shows that brittleness is improved further further, if use of use of \*\*\*\*, low degree-of-polymerization polyvinyl alcohol, and high-polymer polyvinyl alcohol is used together.

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(54)【発明の名称】 インクジェット記録用紙

(57)【要約】

【課題】 親水性バインダー中に分散された固体微粒子を含有する高インク吸収性を有し、低湿下で保存した場合であっても皮膜の脆弱性が低下せず高画質のインクジェット記録が可能なインクジェット記録用紙の提供。

【解決手段】 支持体上に固体微粒子およびポリビニルアルコールを含有する少なくとも1層のインク吸収層を有し、該インク吸収層の少なくとも1層が、ポリビニルアルコールの総量に対して固体微粒子を重量比で2~200倍含有するインクジェット記録用紙において、該固体微粒子を含有する層が平均重合度が1000以下のポリビニルアルコールと平均重合度が2000以上のポリビニルアルコールを含有することを特徴とするインクジェット記録用紙。

## 【特許請求の範囲】

【請求項1】 支持体上に固体微粒子およびポリビニルアルコールを含有する少なくとも1層のインク吸収層を有し、該インク吸収層の少なくとも1層が、ポリビニルアルコールの総量に対して固体微粒子を重量比で2～200倍含有するインクジェット記録用紙において、該固体微粒子を含有する層が平均重合度が1000以下のポリビニルアルコールと平均重合度が2000以上のポリビニルアルコールを含有することを特徴とするインクジェット記録用紙。

【請求項2】 前記固体微粒子が、それぞれ1次粒子の平均粒径が7～80nmのシリカ、炭酸カルシウム、アルミナまたはアルミナ水和物もしくは珪酸マグネシウムから選ばれた固体微粒子であることを特徴とする請求項1に記載のインクジェット記録用紙。

【請求項3】 前記固体微粒子が、1次粒子の平均粒径が7～30nmの気相法により合成されたシリカであることを特徴とする請求項1に記載のインクジェット記録用紙。

【請求項4】 前記平均重合度が1000以下のポリビニルアルコールの量が、平均重合度が2000以上のポリビニルアルコールに対して、重量比で1～30重量%であることを特徴とする請求項1～3のいずれか1項に記載のインクジェット記録用紙。

【請求項5】 支持体上に固体微粒子およびポリビニルアルコールを親水性バインダーとして少なくとも含有するインク吸収層を少なくとも1層有し、該インク吸収層の少なくとも1層の親水性バインダーに対する固体微粒子の重量比が2～200倍であるインクジェット記録用紙であり、該インク吸収層が融点が40℃以下の疎水性有機化合物またはガラス転移温度が40℃以下のポリマーラテックスから選ばれた油滴を固体微粒子に対して5～50重量%含有することを特徴とするインクジェット記録用紙。

【請求項6】 前記油滴の平均粒径が0.05～0.5μmであることを特徴とする請求項5に記載のインクジェット記録用紙。

【請求項7】 前記固体微粒子が、それぞれ1次粒子の平均粒径が7～80nmのシリカ、炭酸カルシウム、アルミナまたはアルミナ水和物もしくは珪酸マグネシウムから選ばれた固体微粒子であることを特徴とする請求項5又は6に記載のインクジェット記録用紙。

【請求項8】 前記固体微粒子が、1次粒子の平均粒径が7～30nmの気相法により合成されたシリカであることを特徴とする請求項5又は6に記載のインクジェット記録用紙。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、水性インクを用いて記録を行なうインクジェット記録用紙に関し、特にイン

ク吸収性を改善したインクジェット記録用紙に関するものである。

## 【0002】

【従来の技術】 インクジェット記録は、インクの微小液滴を種々の作動原理により飛翔させて紙などの記録シートに付着させ、画像・文字などの記録を行うものであるが、比較的高速、低騒音、多色化が容易である等の利点を有している。この方式で従来から問題となっていたノズルの目詰まりとメンテナンスについては、インクおよび装置の両面から改良が進み、現在では各種プリンタ、ファクシミリ、コンピューター端末等、さまざまな分野に急速に普及している。

【0003】 このインクジェット記録方式で使用されるインクジェット記録用紙としては、印字ドットの濃度が高く、色調が明るく鮮やかであること、インクの吸収が早く印字ドットが重なった場合に於いてもインクが流れ出したり滲んだりしないこと、印字ドットの横方向への拡散が必要以上に大きくなく、かつ周辺が滑らかでなければならないこと等が要求される。

20 【0004】 特にインク吸収速度が遅い場合には、2色以上のインク液滴が重なって記録される際に、インクジェット記録用紙上で液滴がハジキ現象を起こしてムラになったり、また、異なる色の境界領域でお互いの色が滲んだりして画質を大きく低下させやすいために、インクジェット記録用紙としては高いインク吸収性を持たせるようにすることが必要である。

【0005】 これらの問題を解決するために、従来から非常に多くの技術が提案されている。

【0006】 例えば、特開昭52-53012号公報に記載されている低サイズ原紙に表面加工用の塗料を湿润させたインクジェット記録用紙、特開昭55-5830号に記載されている支持体表面にインク吸収性の塗層を設けたインクジェット記録用紙、特開昭56-157号公報に記載されている被覆層中の顔料として非膠質シリカ粉末を含有するインクジェット記録用紙、特開昭57-107878号に記載されている無機顔料と有機顔料を併用したインクジェット記録用紙、特開昭58-110287号公報に記載されている2つの空孔分布ピークを有するインクジェット記録用紙、特開昭62-1111782号に記載されている上下2層の多孔質層からなるインクジェット記録用紙、特開昭59-68292号、同59-123696号および同60-18383号公報などに記載されている不定形亀裂を有するインクジェット記録用紙、特開昭61-135786号、同61-148092号および同62-149475号公報等に記載されている微粉末層を有するインクジェット記録用紙、特開昭63-252779号、特開平1-108083号、同2-136279号、同3-65376号および同3-27976号等に記載されている特定の物性値を有する顔料や微粒子シリカを含有するインクジェット記録用紙に関するものである。

ト記録用紙、特開昭57-14091号、同60-219083号、同60-210984号、同61-20797号、同61-188183号、特開平5-278324号、同6-92011号、同6-183134号、同7-137431号、同7-276789号等に記載されているコロイド状シリカ等の微粒子シリカを含有するインクジェット記録用紙、および特開平2-276671号公報、同3-67684号公報、同3-215082号、同3-251488号、同4-67986号、同4-263983号および同5-16517号公報などに記載されているアルミナ水和物微粒子を含有するインクジェット記録用紙等が多数が知られている。

【0007】中でも、インク受容層がインクを吸収したり保持するための空隙を多く有する層（以下、空隙層という）である場合にインク吸収性が良好で境界部の滲みが少なく、高品質な画像が記録できる。

【0008】しかもこの空隙が保存中に特に高温高湿下でその容量が変わったりすることがあるために、空隙層内に空隙が変化しないような固体微粒子を含んでいることが好ましい。

【0009】空隙層内に固体微粒子を含有させて空隙を形成させる場合には、親水性バインダを含有させておくことが安定な皮膜を形成するために必要である。しかしながら、親水性バインダーの固体微粒子に対する添加量は多すぎると、固体微粒子自身あるいは固体微粒子間に形成させる空隙を塞いでしまったり、あるいはインク吸収時にこの親水性バインダー自身がインク吸収初期に膨潤して空隙層を塞いでインク吸収性を低下させる等の問題があり、その使用量は限定される。

【0010】本発明者らの検討によれば、固体微粒子に対する親水性バインダーの添加量の比率は重量比で概ね2~200倍にすることが必要であることがわかつている。

【0011】この様な高い比率の固体微粒子を含有する層はしかしながら皮膜の脆弱性が劣るという欠点を有しており、特に低温下で保存した場合にインク吸収層の表面に微細なヒビワレ状態を発生する。この様なインクジェット記録用紙にインクジェット記録を行った場合には、インクがこのひび割れた線に沿って拡がり著しく画質を低下させてしまう。

【0012】

【発明が解決しようとする課題】本発明は上記の実態に鑑みてなされたものであって、本発明の目的は、親水性バインダー中に分散された固体微粒子を含有する高インク吸収性を有し、低温下で保存した場合であっても皮膜の脆弱性が低下せず高画質のインクジェット記録が可能なインクジェット記録用紙を提供することにある。

【0013】

【課題を解決するための手段】本発明の上記目的は以下の構成により達成される。

【0014】1. 支持体上に固体微粒子およびポリビニルアルコールを含有する少なくとも1層のインク吸収層を有し、該インク吸収層の少なくとも1層が、ポリビニルアルコールの総量に対して固体微粒子を重量比で2~200倍含有するインクジェット記録用紙において、該固体微粒子を含有する層が平均重合度が1000以下のポリビニルアルコールと平均重合度が2000以上のポリビニルアルコールを含有することを特徴とするインクジェット記録用紙。

【0015】2. 前記固体微粒子が、それぞれ1次粒子の平均粒径が7~80nmのシリカ、炭酸カルシウム、アルミナまたはアルミナ水和物もしくは珪酸マグネシウムから選ばれた固体微粒子であることを特徴とする前記1に記載のインクジェット記録用紙。

【0016】3. 前記固体微粒子が、1次粒子の平均粒径が7~30nmの気相法により合成されたシリカであることを特徴とする前記1に記載のインクジェット記録用紙。

【0017】4. 前記平均重合度が1000以下のポリビニルアルコール量が、平均重合度が2000以上のポリビニルアルコールに対して、重量比で1~30重量%であることを特徴とする前記1~3のいずれか1項に記載のインクジェット記録用紙。

【0018】5. 支持体上に固体微粒子およびポリビニルアルコールを親水性バインダーとして少なくとも含有するインク吸収層を少なくとも1層有し、該インク吸収層の少なくとも1層の親水性バインダーに対する固体微粒子の重量比が2~200倍であるインクジェット記録用紙であり、該インク吸収層が融点が40℃以下の疎水性有機化合物またはガラス転移温度が40℃以下のポリマーラテックスから選ばれる油滴を固体微粒子に対して5~50重量%含有することを特徴とするインクジェット記録用紙。

【0019】6. 前記油滴の平均粒径が0.05~0.5μmであることを特徴とする前記5に記載のインクジェット記録用紙。

【0020】7. 前記固体微粒子が、それぞれ1次粒子の平均粒径が7~80nmのシリカ、炭酸カルシウム、アルミナまたはアルミナ水和物もしくは珪酸マグネシウムから選ばれた固体微粒子であることを特徴とする前記5又は6に記載のインクジェット記録用紙。

【0021】8. 前記固体微粒子が、1次粒子の平均粒径が7~30nmの気相法により合成されたシリカであることを特徴とする前記5又は6に記載のインクジェット記録用紙。

【0022】以下、本発明を詳細に説明する。

【0023】本発明のインクジェット記録用紙が含有する固体微粒子は、インクジェット記録用紙で從来公知の固体微粒子を使用することが出来るが無機微粒子が好ましい。

【0024】この目的で用いられる無機微粒子としては、インクジェットで公知の例えは、軽質炭酸カルシウム、重質炭酸カルシウム、炭酸マグネシウム、カオリン、クレー、タルク、硫酸カルシウム、硫酸バリウム、二酸化チタン、酸化亜鉛、水酸化亜鉛、硫化亜鉛、炭酸亜鉛、ハイドロタルサイト、珪酸アルミニウム、ケイソウ土、珪酸カルシウム、珪酸マグネシウム、合成非晶質シリカ、コロイダルシリカ、アルミナ、コロイダルアルミナ、擬ペーマイト、水酸化アルミニウム、リトボン、ゼオライト、水酸化マグネシウム等の白色無機顔料等を使用する事が出来る。

【0025】その様な無機微粒子は、1次粒子のままでバインダー中に均一に分散された状態で用いられることも、また、2次凝集粒子を形成してバインダー中に分散された状態で添加されても良い。

【0026】一方有機微粒子の例としては、ポリスチレン、ポリアクリル酸エステル類、ポリメタクリル酸エステル類、ポリアクリルアミド類、ポリエチレン、ポリブロビレン、ポリ塩化ビニル、ポリ塩化ビニリデン、またはこれらの共重合体、尿素樹脂、またはメラミン樹脂等が挙げられる。

【0027】本発明では空隙率が比較的高い空隙層が得られる点から無機の固体微粒子を用いるのが好ましい。中でも、高い光沢性と高い画像濃度が得られやすいという点から、固体微粒子が、シリカ、炭酸カルシウム、アルミナまたはアルミナ水和物もしくは珪酸マグネシウムから選ばれた固体微粒子であることが好ましい。

【0028】本発明のインクジェット記録用紙で好ましく用いられるシリカ系微粒子としては、従来インクジェットで公知の各種のシリカ系微粒子を使用することが出来る。

【0029】例えば、湿式または気相法で合成された合成シリカ、コロイダルシリカ、1次粒子が凝集して2次粒子を形成している多孔質シリカ任意の形状のシリカを使用する事が出来る。その様な例として、例えば特開昭55-51583号および同56-148583号等に記載された合成非晶質シリカ、例えば特開昭60-204390号に記載された気相法により合成されたシリカ超微粒子、特開昭60-222282号に記載されたフッ素を含有する合成不定形シリカ、特開昭60-224580号および同62-178384号に記載されたシランカップリング剤により表面処理された合成不定形シリカ、例えば特開昭62-183382号および同63-104878号に記載された球状シリカ、特開昭63-317381号に記載されたNa<sub>2</sub>O含有量が0.5重量%以上である合成シリカ微粒子、特開平1-115677号に記載された比表面積が100m<sup>2</sup>/g以上の合成シリカ微粒子、特開昭62-286787号に記載されたアルミナ表面処理された合成シリカ微粒子、特開平1-259982号に記載されたCa、Mgまたは

Ba等の塩で表面処理された合成シリカ微粒子、吸油量が180ml/g以上の合成シリカ微粒子、特開昭57-14091号に記載されたコロイダルシリカ、特開昭60-219084号、特開平6-92011号、同6-297830号および同7-81214号に記載されたカチオン性コロイダルシリカ、および特開平5-278324号および同7-81214号に記載された数珠状に連結したまたは分岐したコロイダルシリカ等を挙げることが出来る。

【0030】しかしながら、高い光沢性と高い空隙量を得るためにには、平均粒径が7~80nmの超微粒子シリカを用いることが好ましい。このシリカ微粒子は表面をカチオン変成されたものであってもよく、また、Al、Ca、MgおよびBa等で処理された物であってもよい。

【0031】本発明のインクジェット記録用紙で好ましく用いられる炭酸カルシウムとしては、例えば、特開昭57-12486号、同57-129778号、同58-55283号、同61-20792号に記載された特定に比表面積を有する軽質炭酸カルシウム、特開昭63-57277号及び特開平4-250091号に記載された針柱状炭酸カルシウム、特開平3-251487号に記載された特定の針状1次粒子が凝集して2次粒子を形成した炭酸カルシウム微粒子、特開平4-250091号及び同4-260092号に記載された特定の吸油量を有する針柱状の斜方晶アルゴナイト炭酸カルシウム、および特開平7-40648号に記載された球状沈降性炭酸カルシウム等が挙げられる。

【0032】この場合、高い光沢性と高い空隙量を得られることから、粒径が約7~80nmの炭酸カルシウム微粒子を使用することが好ましい。

【0033】本発明で好ましく用いられる珪酸マグネシウムは不定形粒子、球状、板状のいずれであっても良いが板状が好ましい。板状珪酸マグネシウムの平均粒子径は板状の平均投影面積を求めこれを円に換算したときの直径を表し、7~80nmの微粒子が好ましい。

【0034】本発明で好ましく用いられるアルミナまたはアルミナ水和物は結晶性であっても、非晶質であっても良く、また、形状は不定形粒子、球状粒子、針状粒子など任意の形状の物を使用することが出来る。

【0035】上記各種の無機固体微粒子の平均粒子径は、それを電子顕微鏡で撮影したときの平均投影面積を測定し、これを円に換算したときの直径を表す。

【0036】本発明で好ましく用いられる上記固体微粒子は特に1次粒子の平均粒径が7~80nmのものであることが好ましい。

【0037】1次粒子径が7nm未満の場合には、取り扱い性が難しく、また、80nmを超える場合には光沢の低下が顕著になりやすい。

【0038】上記固体微粒子含有層は皮膜形成の点で親

水性バインダーを含有することが本発明のインクジェット記録用紙では必要である。

【0039】一般にインクジェット記録用紙に用いられる親水性バインダーとしては、ゼラチンまたはゼラチン誘導体、ポリビニルピロリドン（平均分子量が約20万以上が好ましい）、フルラン、ポリビニルアルコールまたはその誘導体（平均分子量が約2万以上が好ましい）、ポリエチレングリコール（平均分子量が10万以上が好ましい）、カルボキシメチルセルロース、ヒドロキシエチルセルロース、デキストラン、デキストリン、ポリアクリル酸およびその塩、寒天、 $\kappa$ -カラギーナン、 $\lambda$ -カラギーナン、 $\iota$ -カラギーナン、キサンテンガム、ローカストビーンガム、アルギン酸、アラビアゴム、フルラン、特開平7-195826号および同7-9757号に記載のポリアルキレンオキサイド系共重合性ポリマー、水溶性ポリビニルピラール、あるいは、特開昭62-245260号に記載のカルボキシル基やスルホン酸基を有するビニルモノマーの単独またはこれらのビニルモノマーを繰り返して有する共重合体等のポリマー等が知られているが本発明においては、ポリビニルアルコールを少なくとも含有することが高いインク吸収性と光沢性、更にはカールの抑制や高湿下でのベタッキ防止の観点で必要である。

【0040】ここでいうポリビニルアルコールには、ポリ酢酸ビニルの部分ケン化物または完全ケン化物等通常言わわれているポリビニルアルコール以外に、カチオン変性されたポリビニルアルコールも含有される。

【0041】上記ポリ酢酸ビニルのケン化度は60～100%、好ましくは70～99%のものが本発明では用いられる。

【0042】また、好ましいカチオン変性されたポリビニルアルコールは、カチオン性基を有するエチレン性不飽和单量体と酢酸ビニルとの共重合体をケン化することにより得られる。

【0043】カチオン性基を有するエチレン性不飽和单量体としては、例えばトリメチル-（2-アクリルアミド-2, 2-ジメチルエチル）アンモニウムクロライド、トリメチル-（3-アクリルアミド-3, 3-ジメチルプロピル）アンモニウムクロライド、N-ビニルイミダゾール、N-ビニル-2-メチルイミダゾール、N-（3-ジメチルアミノプロピル）メタクリルアミド、ヒドロキシルエチルトリメチルアンモニウムクロライド、トリメチル-（-メタクリルアミドプロピル）アンモニウムクロライド、N-（1, 1-ジメチル-3-ジメチルアミノプロピル）アクリルアミド等が挙げられる。

【0044】カチオン変性ポリビニルアルコールのカチオン変性基含有单量体の比率は、酢酸ビニルに対して0.1～10モル%が好ましく、より好ましくは0.2～5モル%である。また、カチオン変性ポリビニルアル

コールのケン化度は60～100%が好ましく、より好ましくは70～99%である。

【0045】本発明のインクジェット記録用紙において、空隙層を形成する固体微粒子の親水性バインダーに対する比率は重量比で、2～200倍であることが必要である。2倍未満の時は形成される空隙比率が小さく最大インク量を完全に吸収するためには膜厚が厚すぎることに伴う諸々の問題が生じやすくなったり、また、親水性バインダーがインク吸収時に膨潤して空隙層のインク吸収速度を低下させ、得られる画質を低下させる。

【0046】一方、200倍を越える場合には、後述の種々の手段を採用したとしても皮膜の脆弱性が大きく劣化して高画質のインクジェット記録が出来なくなる。

【0047】好ましい比率は、2.5～100倍、特に好ましい比率は3～50倍である。

【0048】また、固体微粒子として、特に好ましい気相法シリカを用いた場合には、好ましい比率は3～20である。

【0049】本発明のインクジェット記録用紙の空隙層は親水性バインダーに対して特に高い比率の固体微粒子を含有するためにこれに伴う皮膜脆弱性を改善するために前記の如く、

20 ①該固体微粒子含有層が平均重合度が1000以下のポリビニルアルコールと平均重合度が2000以上のポリビニルアルコールを含有するか、あるいは、  
②固体微粒子含有層が油滴を固体微粒子に対して5～50重量%含有する、かの少なくともいずれか一つが満たされることが必要である。

【0050】上記、①において、クラックを生じにくい安定な皮膜の形成のためにはより高重合度のポリビニルアルコールを使用するのが好ましく、この観点からは平均重合度が2000以上のポリビニルアルコールを単独で使用することである程度は良好な皮膜が得られる。逆に低分子量のポリビニルアルコールのみを使用した場合には、特に固体微粒子を多く含有する皮膜においては塗布後の乾燥過程でクラックが生じやすい。

【0051】しかしながら、平均重合度が2000以上のポリビニルアルコールのみを使用した場合には、皮膜の微小のクラックが完全にはなくならず、また、塗布乾燥後に高温下で保存した場合に皮膜の脆弱性が低下し、特に低湿度条件下で皮膜にひび割れが生じやすくなる。

【0052】この問題は平均重合度の高いポリビニルアルコールに、平均重合度が1000以下の低重合度ポリビニルアルコールを併用することで改良されることを本発明者らは見いだして第1の本発明に到ったものである。

【0053】平均重合度が2000以上のポリビニルアルコールの中でも特に平均重合度が3000以上のものが好ましい。平均重合度の上限は皮膜の脆弱性改良の点からは限定されないが、一般に高重合度化するにつれて

ポリビニルアルコールの溶解性が低下して目的とする濃度の液が出来にくくなるため、平均重合度は一般には5000以下、特に4000以下が好ましい。

【0054】一方平均重合度が1000以下のポリビニルアルコールの内好ましいのは、平均重合度が500以下、特に400以下が最も好ましい。

【0055】平均重合度の下限は、特に限定されないが通常は200以上である。

【0056】平均重合度が1000以下のポリビニルアルコールの量が、平均重合度が2000以上のポリビニルアルコールに対して、重量比で1～30%であることが好ましい。1%未満である場合には本発明の効果が実質的に得られにくくなり、また、30%を超えると塗布乾燥後の皮膜の形成性が悪化しやすくなり、特にクラック形成が増大したり支持体との接着性が低下しやすくなる。特に好ましい範囲は2～20%である。

【0057】上記②において、インク吸収層が含有する油滴としては、大きく2種類のものに分けられる。

【0058】その第1は、前記油滴が、融点が40℃以下の疎水性有機化合物を有する油滴である場合であり、第2のものは前記油滴が、ガラス転移温度が40℃以下のポリマーラテックスである場合である。

【0059】第1のタイプの油滴は通常、室温で水に対する溶解度が0.1%重量%以下、特に好ましくは0.01重量%以下であって融点が40℃以下の疎水性有機化合物である。

【0060】そのような疎水性有機化合物は通常の疎水性高沸点有機溶媒として知られている有機化合物や、融点が40℃以下の疎水性ポリマーが挙げられる。

【0061】上記疎水性有機化合物としては、例えばタル酸エステル類（例えばジブチルフタレート、ジオクチルフタレート、ジイソデシルフタレート等）、リン酸エステル類（例えば、トリクロレジルホスフェート、トリオクチルfosfate等）、脂肪酸エステル類（ステアリン酸ブチル、セバチン酸ビス（2-エチルヘキシル）、エチレングリコールジステアレート、グリセロールトリブチレート等）、アミド類（N,N-ジエチルラウリルアミド、N,N-ジエチル-2-(2,5-ジエターミルフェノキシ)ブタニアミド等）、エーテル類（エチレングリコールジブチルエーテル、デシルエーテル、ジベンジルエーテル等）、シリコンオイルおよび流動パラフィン等を挙げることが出来る。

【0062】また、融点が40℃以下の疎水性ポリマーとしては、例えば、ポリ(2-エチルヘキシルメタクリレート)、ポリブチルメタクリレート、コポリ(ブチルアクリレート/ヒドロキシルエチルメタクリレート:90/10)、ポリビニルアセテート、ポリビニルプロピオネート、コポリ(ブチルアクリレート/t-ブチルアクリレート/2-エチルヘキシルメタクリレート/ステレン:60/20/10/10)等が挙げられる。

【0063】上記疎水性ポリマーとしては平均分子量が5000～10万程度のポリマーが好ましく用いられる。10万を超えるポリマーの場合、後述する乳化分散等の方法で微粒子の油滴を形成しにくくなる。

【0064】上記疎水性有機化合物は高速ホモジナイザーや高圧ホモジナイザ等により親水性バインダー中に、好ましくは界面活性剤の存在下で乳化分散されて用いられる。この際、酢酸エチル、酢酸プロピル、メチルエチルケトン、アセトン、N,N-ジメチルホルムアミド等の低沸点有機溶媒等の存在下で乳化分散するのがより微小な油滴を形成するのに好ましい。

【0065】また、この乳化分散時に、他の疎水性有機化合物（例えば紫外線吸収剤や蛍光増白剤、画像安定剤等）で融点が40℃を超える有機化合物を併用することもできるが、好ましくは油滴を形成する有機化合物の50重量%以上は融点が40℃以下の化合物であるのが好ましい。

【0066】一方、第2のガラス転移温度が40℃以下のポリマーラテックスは、乳化重合法で重合されたポリマーラテックスであり、例えば、スチレン-ブタジエン共重合体ラテックス、ポリアクリル酸エステル系ラテックス、ポリメタクリル酸エステル系ラテックス、酢酸ビニル系ラテックス、エチレン-酢酸ビニル系ラテックス等が好ましく用いられる。

【0067】上記の重合体ラテックスの例としては例えば、スチレン/ブタジエンラテックス(7/3)、ポリ酢酸ビニルラテックス、酢酸ビニル/エチレンラテックス(9/1)、酢酸ビニル/メタクリル酸エチルラテックス(5/5)、塩化ビニル/アクリル酸エチル(3/2)、アクリル酸エチル/アクリル酸メチル/HEMA(5/4/1)、スチレン/アクリル酸ブチル/HEMA(1/6/3)、シリコンラテックス等を挙げることが出来る。上記において、共重比率はモル比を表し、HEMAはヒドロキシルエチルメタクリレートを表す。

【0068】上記各種の油滴の平均粒径は0.05～0.5μmであることが好ましい。油滴のサイズが0.05μm以下である場合には油滴が不安定になりやすくなったり、脆弱性の改良効果が低減しやすくなる。また、油滴のサイズが0.5μmを超える場合には光沢が低下しやすくなる。

【0069】上記油滴はインク吸収層が含有する固体微粒子に対して5～50重量%使用するのが本発明の効果を得るのに必要である。

【0070】油滴の固体微粒子に対する比率が5重量%未満である場合には、皮膜の脆弱性の改良効果が不十分であり、また、50重量%を超える場合には空隙比率が低下してインク吸収容量が低下したり光沢の低下が起こりやすい。

【0071】特に好ましい使用量は10～40重量%である。

【0072】本発明のインクジェット記録用紙は、固体微粒子および親水性バインダーを含有するインク吸収層を2層以上有していることもできる。この場合、これら複数のインク吸収層に使用される親水性バインダーや固体微粒子の種類あるいは比率は任意に選択されるが、少なくとも1層は親水性バインダーに対する固体微粒子の比率が2～200倍になっている層が有る場合については、該層に平均重合度が本発明の如く異なる2種類のポリビニルアルコールを併用するかまたは本発明の油滴を添加することが必要である。

【0073】特に本発明の効果を最大限に引き出すためには、上記平均重合度の異なるポリビニルアルコールを用いることと油滴を使用することを併用することである。

【0074】本発明のインクジェット記録用紙は、前述の固体微粒子および親水性バインダーを含有する少なくとも1層のインク吸収層を有するが、この固体微粒子含有層以外にも親水性バインダー層を有することができる。その様な親水性バインダー層は固体微粒子を有していてもいなくても良いが、空隙層で無い場合には好ましくは本発明の固体微粒子含有層より支持体から離れた側に設けられる際には乾燥膜厚が2μm以下、好ましくは1.5μm以下になるようにするのがインク吸収速度の点から好ましい。

【0075】本発明のインクジェット記録用紙のインク受容性層側の任意の層中には、必要に応じて各種の添加剤を含有させることができる。

【0076】例えば、特開昭57-74193号公報、同57-87988号公報及び同62-261476号公報に記載の紫外線吸収剤、特開昭57-74192号、同57-87989号公報、同60-72785号公報、同61-146591号公報、特開平1-95091号公報及び同3-13376号公報等に記載されている退色防止剤、アニオン、カチオンまたはノニオンの各種界面活性剤、特開昭59-42993号公報、同59-52689号公報、同62-280069号公報、同61-242871号公報および特開平4-219266号公報等に記載されている蛍光増白剤、硫酸、リン酸、クエン酸、水酸化ナトリウム、水酸化カリウム、炭酸カリウム等のpH調整剤、消泡剤、ジエチレングリコール等の潤滑剤、防腐剤、増粘剤、硬膜剤、帯電防止剤、マット剤等の公知の各種添加剤を含有させることもできる。

【0077】硬膜剤としては無機または有機の硬膜剤を使用することが出来、例えばクロムみょうばん、ホルムアルデヒド、グリオキサール、エポキシ系化合物、ビニルスルホン系化合物、アクリロイル系化合物、s-トリアジン系化合物、N-メチロール系化合物、カルボジイミド系化合物、およびエチレンイミノ系化合物等を使用することが出来る。

【0078】本発明のインクジェット記録用紙におけるインク記録面側の塗布固形分の量は特に制限はないが、概ね10～40g/m<sup>2</sup>が好ましく、20～30g/m<sup>2</sup>がより好ましい。なお、記録画像形成後のカールの防止という面からは、なるべく薄く形成するのが良い。

【0079】本発明のインク記録面側の任意の構成層中には、画像の耐水化剤として特開昭56-84992号公報のポリカチオン高分子電解質、特開昭57-36692号公報の塩基性ラテックスポリマー、特開昭61-58788号公報、同62-174184号公報等記載のポリアリルアミン、特開昭61-47290号公報記載のアルカリ金属弱酸塩等を一種以上用いることができる。

【0080】本発明のインクジェット記録用紙に用いられる支持体としては、従来インクジェット用記録用紙として公知のものを適宜使用できる。

【0081】透明支持体としては、例えば、ポリエスチル系樹脂、ジアセテート系樹脂、トリアテセート系樹脂、アクリル系樹脂、ポリカーボネート系樹脂、ポリ塩化ビニル系樹脂、ポリイミド系樹脂、セロハン、セルロイド等の材料からなるフィルムや板、およびガラス板などを挙げられ、この中でもOHPとして使用されたときの輻射熱に耐える性質のものが好ましく、ポリエチレンテレフタレートが特に好ましい。このような透明な支持体の厚さとしては、約10～200μmが好ましい。

【0082】また、透明である必要のない場合に用いる支持体としては、例えば、一般の紙、合成紙、樹脂被覆紙、布、木材、金属等からなるシートや板、および上記の透光性支持体を公知の手段により不透明化処理したものの等を挙げることができる。不透明の支持体としては、基紙の少なくとも一方に白色顔料等を添加したポリオレフィン樹脂被覆層を有する樹脂被覆紙（いわゆるRCペーパー）、ポリエチレンテレフタレートに白色顔料を添加してなるいわゆるホワイトペーパーが好ましい。

【0083】本発明の効果は、特に支持体が非吸水性である場合に効果が大きく、特に透明または不透明のポリエチレンテレフタレート支持体や原紙の両面をポリエチレンなどの疎水性樹脂で被覆した支持体が好ましく用いられる。

【0084】支持体とインク受像層の接着強度を大きくする等の目的で、インク受容層の塗布に先立って、支持体にコロナ放電処理や下引処理等を行うことが好ましい。さらに、本発明のインクジェット記録用紙は必ずしも無色である必要はなく、着色された記録シートであつてもよい。

【0085】本発明のインクジェット記録用紙を製造するに当たっては、インク受容性層を含む各親水性層を支持体上に塗布する方法は公知の方法から適宜選択して行うことが出来る。

【0086】塗布方式としては、ロールコーティング

法、ロッドバーコーティング法、エアナイフコーティング法、スプレーコーティング法、カーテン塗布方法あるいは米国特許第2,681,294号公報記載のホッパーを使用するエクストルージョンコート法が好ましく用いられる。

【0087】本発明で言う水性インクとは、下記着色剤及び液媒体、その他の添加剤から成る記録液体である。着色剤としてはインクジェットで公知の直接染料、酸性染料、塩基性染料、反応性染料あるいは食品用色素等の水溶性染料が使用できる。

【0088】水性インクの溶媒としては、水及び水溶性の各種有機溶剤、例えば、メチルアルコール、イソプロピルアルコール、n-ブチルアルコール、tert-ブチルアルコール、イソブチルアルコール等のアルコール類；ジメチルホルムアミド、ジメチルアセトアミド等のアミド類；アセトン、ジアセトンアルコール等のケトンまたはケトンアルコール類；テトラヒドロフラン、ジオキサン等のエーテル類；ポリエチレンジコール、ポリプロピレンジコール等のポリアルキレンジコール類；エチレンジコール、プロピレンジコール、ブチレンジコール、トリエチレンジコール、1,2,6-ヘキサントリオール、オオジグリコール、ヘキシレンジグリコール、ジエチレンジコール、グリセリン、トリエタノールアミン等の多価アルコール類；エチレンジコールメチルエーテル、ジエチレンジコールメチル（又はエチル）エーテル、トリエチレンジコールモノブチルエーテル等の多価アルコールの低級アルキルエーテル類等が挙げられる。

【0089】これらの多くの水溶性有機溶剤の中でも、

塗布液-1

純水（イオン交換水）  
エタノール 30ml  
シリカ（平均1次粒子径が13nmの気相法シリカ）  
ポリビニルアルコール  
(平均重合度=3500、ケン化度=8.8%)

界面活性剤（AS-1）

AS-1：トリイソプロピルナフタレンスルホン酸ナトリウム

次に、インクジェット記録用紙-1において、表1に示すように本発明の疎水性有機化合物を添加および比較の有機化合物を添加したインクジェット記録用紙をインクジェット記録用紙-1と同様にしてインクジェット記録用紙-2～11を作製した。但し油滴の添加に伴い塗布液の全量は各インクジェット記録用紙で同じになるよう

ジエチレンジリコール、トリエタノールアミンやグリセリン等の多価アルコール類、トリエチレンジリコールモノブチルエーテルの多価アルコールの低級アルキルエーテル等が好ましいものである。

【0090】その他の水性インクの添加剤としては、例えばpH調節剤、金属封鎖剤、防カビ剤、粘度調整剤、表面張力調整剤、潤滑剤、界面活性剤、及び防錆剤等が挙げられる。

【0091】水性インク液はインクジェット記録用紙に対する濡れ性が良好にするために、20°Cにおいて、25～60dynes/cmであることが好ましく、より好ましくは30～50dynes/cmの範囲内の表面張力を有するのが好ましい。

【0092】

【実施例】本発明を実施例を挙げて具体的に説明するが、本発明の実施態様はこれらに限定されるものではない。

【0093】実施例1

160g/m<sup>2</sup>の原紙の両面をポリエチレンで被覆した写真用印画紙支持体（インク吸収層側のポリエチレン層中に12重量%のアナターゼ型酸化チタンを含有）に以下の塗布液-1を潤滑膜厚が190μmになるように塗設して乾燥してインクジェット記録用紙-1を作製した。

【0094】塗布はスライドホッパー方式で行い、塗布後、約10°Cに冷却してこの温度の風で1分間乾燥した後、30°C～45°Cの風で4分間かけて乾燥した。

【0095】

塗布液-1	950ml
エタノール	50ml
シリカ	51g
ポリビニルアルコール	8g
AS-1	0.1g

に純水で調整した。また、上記各疎水性化合物はポリビニルアルコール中で界面活性剤としてAS-1の存在下で乳化分散して添加した。

【0096】

【表1】

記録用紙	添加剤(融点)	油滴径	添加量
2 (比較例)	流動パラフィン ( $mp < 10^{\circ}\text{C}$ )	0.3 $\mu\text{m}$	3%
3 (本発明)	"	"	10%
4 (本発明)	"	"	30%
5 (比較例)	"	"	90%
6 (比較例)	D I D P ( $mp = -53^{\circ}\text{C}$ )	0.32 $\mu\text{m}$	3%
7 (本発明)	"	"	10%
8 (本発明)	"	"	30%
9 (比較例)	"	"	90%
10 (比較例)	固体パラフィン ( $mp = 60^{\circ}\text{C}$ )	0.38 $\mu\text{m}$	20%
11 (比較例)	D P P ( $mp = 74^{\circ}\text{C}$ )	0.28 $\mu\text{m}$	20%

D I D P : ジイソデシルフタレート

D P P : ジフェニルフタレート

表中、添加量はシリカに対する重量比で表した。

記録用紙 : インクジェット記録用紙

【0097】得られた各々のインクジェット記録用紙について、インク吸収性、皮膜脆弱性および光沢性を以下に記す方法で評価した。なおインク吸収性はセイコーエプソン株式会社製インクジェットプリンターM J - 900Cを用いた。

【0098】(1) インク吸収性: イエローおよびシアンのそれぞれ最大インク量が40%になるように均一に吐出させて記録し、ベタ部の赤色反射濃度をマイクロデシットメーター(アパー チュア = 200  $\mu\text{m}$ )を用いて20点測定し、その濃度のバラツキの標準偏差を求め平均反射濃度で割った値を求めた。

【0099】インク吸収性が良好な場合には画像にムラが無くこの値が小さくなるが、インク吸収性が低下するとこのお互いのインク液滴同士が記録紙上で互いにビーディングを起こしてムラになりこの値が増加する。

【0100】(2) 皮膜脆弱性: 各々のインクジェット記録用紙を25°C、相対湿度20%で、印字面が外側になるように直径60mmの円筒状にした状態で1昼夜保存した後表面のヒビワレ状態をルーペで観察した。

## 【0101】

◎: ルーペでもひび割れが全くない状態

○: 部分的にひび割れがルーペで見られるが画質上は殆ど影響がない

△: 目視ではひび割れがなくルーペでヒビ割れが認められる、また画質上も悪影響が見られる

×: 目視でひび割れが見られ、しかも画質上の影響が非常に大きい

## (3) 光沢性

記録層面を日本電色工業株式会社製の変角光沢度計(VGS-1001-DP)を用い、75度光沢を測定した。

【0102】得られた結果を表2に示す。

【0103】

【表2】

記録用紙	インク吸収性	脆弱性	光沢
1 (比較例)	0.04	×	61%
2 (比較例)	0.04	×	61%
3 (本発明)	0.05	○	60%
4 (本発明)	0.06	○	58%
5 (比較例)	0.10	○	38%
6 (比較例)	0.04	×	60%
7 (本発明)	0.05	○	61%
8 (本発明)	0.06	○	59%
9 (比較例)	0.11	○	43%
10 (比較例)	0.05	×	46%
11 (比較例)	0.06	×	53%

記録用紙 : インクジェット記録用紙

【0104】表2の結果から、本発明のインクジェット記録用紙である3、4、7、8はインク吸収性を低下させずに皮膜の脆弱性を大きく改善出来、しかも光沢の低下が殆どないことがわかる。

【0105】これに対して、油滴の添加量が本発明以下であるインクジェット記録用紙-2、6はひび割れ改良効果が殆どなく、一方油滴の添加量が本発明以上であるインクジェット記録用紙-5、9ではインクの吸収速度が低下し、又光沢性の低下も大きい。

【0106】一方、融点が40°Cを超える疎水性有機化合物を使用した場合にはひび割れ改良効果が全くない。

## 【0107】実施例2

実施例1のインクジェット記録用紙において、塗布液中にポリマー ラテックスを表3に示すように添加したインクジェット記録用紙-21~28をインクジェット記録用紙-1と同様にして作製した。

【0108】実施例1と同様に評価し、表4に示す結果を得た。

【0109】

【表3】

記録用紙	添加剤 (Tg)	液滴径	添加量
21 (本発明)	ET/VA (Tg<20°C)	0.10 μm	10%
22 (本発明)	"	"	30%
23 (比較例)	"	"	60%
24 (本発明)	ST/BA/HEMA (Tg<20°C)	0.09 μm	10%
25 (本発明)	"	"	30%
26 (比較例)	"	"	60%
27 (比較例)	ST (Tg=100°C)	0.12 μm	20%
28 (比較例)	BMA (Tg=57°C)	0.08 μm	20%

ET/VA : エチレン/酢酸ビニル共重合ラテックス (10/90)

ST/BA/HEMA : スチレン/ブチルアクリレート/ヒドロキシルエチルメク  
リレート共重合ラテックス (20/70/10)

ST : ポリスチレンラテックス

BMA : ポリブチルアクリレート

記録用紙 : インクジェット記録用紙

【0110】

【表4】

記録用紙	インク吸収性	脆弱性	光沢
21 (本発明)	0.05	○	62%
22 (本発明)	0.07	○	64%
23 (比較例)	0.13	◎	48%
24 (本発明)	0.05	○	59%
25 (本発明)	0.06	○	57%
26 (比較例)	0.11	○	45%
27 (比較例)	0.07	×	51%
28 (比較例)	0.08	△	42%

記録用紙 : インクジェット記録用紙

【0111】表4の結果から、油滴としてポリマーラテックスを使用した場合であっても、ガラス転移温度が40°C以下であって、シリカに対して5~50重量%含有したインクジェット記録用紙-21、22、24、25はインク吸収性や光沢性を劣化させることなくひび割れ

【塗布液-1】

純水

980 ml

平均粒径が0.007 μmの気相法微粒子シリカ

48.0 g

平均重合度が3500のポリビニルアルコール

10.8 g

(PVA3500、ケン化度94%)

界面活性剤-1 (AS-1)

1.2 g

次に、この塗布層の上に以下の組成の【塗布液-3】を湿润膜厚が8 μmに成るように塗布乾燥してインクジェ

ット記録用紙-31を得た。

【0115】

【塗布液-2】

純水

800 ml

フェニルカルバモイル化ゼラチン

40 g

(アミノ基封鎖率=88%)

25 g

ポリビニルピロリドン (K-90)

12 g

ポリエチレンオキサイド (平均分子量=約15万)

0.7 g

界面活性剤-2 (AS-2)

2.1 g

硬膜剤-1

AS-2 : スルホカハク酸ジオクチルエステルナトリウム塩

硬膜剤-1 : 1, 5-ジグリジル-3-ヒドロキシベンタン

次にインクジェット記録用紙-31において、表5に示すようなL.P分散物を添加した【塗布液-2】を用い

て、インクジェット記録用紙-31と同様にしてインクジェット記録用紙-32~34を作製した。

【0116】なお、LP分散物の添加時には塗布液の総量が一定になるように純水の量を調整した。

【0117】また、使用したLP分散物は、流動パラフ

記録用紙	分散物	油滴比率(対シリカ)
31(比較例)	—	0%
32(本発明)	LP分散液 60ml	10%
33(本発明)	〃 250ml	42%
34(比較例)	〃 600ml	100%

記録用紙：インクジェット記録用紙

【0119】得られたインクジェット記録用紙を実施例1と同様にして評価した。結果を表6に示す。

【0120】

【表6】

記録用紙	インク吸収性	脆弱性	光沢
31(比較例)	0.10	×	74%
32(本発明)	0.12	△	72%
33(本発明)	0.13	○	68%
34(比較例)	0.19	○	48%

記録用紙：インクジェット記録用紙

【0121】表6に示す結果から、最上層のゼラチンを主体とする膨潤層を設けた場合、インク吸収性は全体に低下するが光沢性は向上する。

【0122】この中でも、本発明のインクジェット記録用紙-32、33はインク吸収性や光沢性の低下が比較

〔塗布液-2a〕

純水

微粒子炭酸カルシウム(平均粒径=約0.03μm)

920ml

120g

平均重合度1700のポリビニルアルコール

6.2g

(ケン化度90%)

界面活性剤-1

1.0g

【0126】

記録用紙	分散物	炭酸カルシウムに対する比率
41(比較例)	—	0%
42(本発明)	D1分散液 60ml	5.0%
43(本発明)	〃 250ml	20.8%
44(比較例)	〃 650ml	54.2%

記録用紙：インクジェット記録用紙

【0127】

【表8】

記録用紙	インク吸収性	脆弱性	光沢
41(比較例)	0.14	×	75%
42(本発明)	0.14	△	74%
43(本発明)	0.15	○	70%
44(比較例)	0.23	○	53%

記録用紙：インクジェット記録用紙

【0128】表8の結果から、微粒子炭酸カルシウムを固体微粒子として使用した場合でも実施例3と同様の効果が得られることがわかる。

【0129】実施例5

実施例1で作製したインクジェット記録用紙-1において、8gのポリビニルアルコール(平均重合度3500)を表9に示すように、高重合度のポリビニルアルコールと低重合度ポリビニルアルコールの組み合わせに変更した以外はインクジェット記録用紙-1と同様にしてインクジェット記録用紙-51~61を作製した。(いずれもポリビニルアルコールの量は同一である。)表中、高重合度PVA及び低重合度PVAはそれぞれ高重合度、低重合度のポリビニルアルコールの量を示す。

【0130】

【表9】

記録用紙	高重合度PVA			低重合度PVA			低重合度比率(%)
	量(g)	ケン化度(%)	重合度	量(g)	ケン化度(%)	重合度	
1(比較例)	8.0	88	3500	0.0	—	—	0%
5 1(本発明)	7.9	88	3500	0.1	88	300	1.3%
5 2(本発明)	7.7	88	3500	0.3	88	300	3.9%
5 3(本発明)	7.0	88	3500	1.0	88	300	14.3%
5 4(本発明)	6.0	88	3500	2.0	88	300	33.3%
5 5(本発明)	7.7	88	3500	0.3	88	500	3.9%
5 6(本発明)	7.7	88	3500	0.3	88	700	3.9%
5 7(比較例)	7.7	88	3500	0.3	88	1100	3.9%
5 8(本発明)	7.7	88	2500	0.3	88	300	3.9%
5 9(比較例)	7.7	88	1750	0.3	88	300	3.9%
6 0(本発明)	7.7	98	3500	0.3	82	300	3.9%
6 1(本発明)	7.5	88	3500	0.3	88	300	4.0%

記録用紙：インクジェット記録用紙

【0131】

【表10】

記録用紙	インク吸収性	脆弱性		光沢
		保存前	加熱保存後	
1(比較例)	0.04	×	×	61%
5 1(本発明)	0.04	○	△	64%
5 2(本発明)	0.04	○	○	69%
5 3(本発明)	0.04	○	○	68%
5 4(本発明)	0.04	○	△	65%
5 5(本発明)	0.05	○	○	61%
5 6(本発明)	0.04	○	△	59%
5 7(比較例)	0.04	×	×	59%
5 8(本発明)	0.04	○	○	58%
5 9(比較例)	0.05	×	×	41%
6 0(本発明)	0.05	○	○	66%
6 1(本発明)	0.05	○	○	65%

記録用紙：インクジェット記録用紙

【0132】表10の結果から、平均重合度が1000以下の低重合度のポリビニルアルコールを、平均重合度2000以上の高重合度のポリビニルアルコールと併用したインクジェット記録用紙(5 1、5 2、5 3、5 4、5 5、5 6、5 8、6 0、6 1)は、加熱処理前後で皮膜の脆弱性が併用しない試料-1に比較して改善されており、特に低重合度ポリビニルアルコールの重合度が500以下であって、高重合度に対する比率が2~20%の試料(5 2、5 3、5 5、5 8、6 0、6 1)が特に良好な脆弱性を有していることがわかる。

【0133】また、高重合度ポリビニルアルコールの平均重合度が3000以上であって低重合度ポリビニルアルコールの平均重合度が400以下の本発明のインクジ

エット記録用紙(5 1~5 4、6 0、6 1)は光沢性が特に優れていることがわかる。

【0134】実施例6

実施例3で作製したインクジェット記録用紙-3 1において、塗布液-1で使用した10.8gのポリビニルアルコール(平均重合度3500)を表11に示すように、高重合度のポリビニルアルコールと低重合度ポリビニルアルコールの組み合わせに変更した以外はインクジェット記録用紙-3 1と同様にしてインクジェット記録用紙-7 1~7 8を作製した(いずれもポリビニルアルコールの量は同一である。)。

【0135】

【表11】

記録用紙	高重合度PVA			低重合度PVA			低重合度比率(%)
	量(g)	ケン化度(%)	重合度	量(g)	ケン化度(%)	重合度	
3 1 (比較例)	10.8	88	3500	0.0	—	—	0%
7 1 (本発明)	10.3	88	3500	0.5	88	300	4.8%
7 2 (本発明)	9.3	88	3500	1.5	88	300	16.1%
7 3 (本発明)	8.8	88	3500	2.0	88	300	22.7%
7 4 (本発明)	8.3	88	3500	2.5	88	300	30.1%
7 5 (本発明)	10.3	88	3500	0.5	88	700	4.8%
7 6 (比較例)	10.3	88	3500	0.5	88	1100	4.8%
7 7 (本発明)	10.8	88	2500	0.5	88	300	4.8%
7 8 (比較例)	10.3	88	1750	0.5	88	300	4.8%

記録用紙：インクジェット記録用紙

【0136】得られた試料を実施例-5と同様に評価し、表12に示す結果を得た。

【0137】

【表12】

記録用紙	インク吸収性	脆弱性		光沢
		保存前	加熱保存後	
3 1 (比較例)	0.10	×	×	74%
7 1 (本発明)	0.11	○	○	75%
7 2 (本発明)	0.10	○	○	73%
7 3 (本発明)	0.10	○	△	69%
7 4 (本発明)	0.11	△	△	65%
7 5 (本発明)	0.11	○	△	70%
7 6 (比較例)	0.10	×	×	67%
7 7 (本発明)	0.11	○	△	71%
7 8 (比較例)	0.10	×	×	50%

記録用紙：インクジェット記録用紙

【0138】表12の結果から、最上層にゼラチンを主体とする薄い膨潤層を設けた場合であっても本発明の効果である脆弱性の改良効果と高い光沢性が本発明のインクジェット記録用紙(71~75・77)で得られることがわかる。

【0139】実施例7

実施例1で作製したインクジェット記録用紙-7において、8gの平均重合度が3500のポリビニルアルコールを、7.5gの平均重合度が3500のポリビニルアルコールと、0.5gの平均重合度が300のポリビニルアルコールの併用に変更した以外はインクジェット記録用紙-7と同様にしてインクジェット記録用紙-80を作製した。実施例1と同様に評価したところ、

インク吸収性: 0.04

脆弱性 : ○  
 光沢性 : 66%  
 という結果を得た。このことから、湯滴の使用と低重合度ポリビニルアルコールと高重合度ポリビニルアルコールの併用を併用すれば、脆弱性が更に一層改善されることがわかる。

【0140】

【発明の効果】実施例で実証した如く、本発明による、インクジェット記録用紙は親水性バインダー中に分散された固体微粒子を含有する高インク吸収性を有し、低湿下で保存した場合であっても皮膜の脆弱性が低下せず高画質のインクジェット記録が可能で優れた効果を有する。

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